

Coupling a nano-particle with isothermal fluctuating hydrodynamics: Coarse-graining from microscopic to mesoscopic dynamics

Pep Español¹, Aleksandar Donev^{2,1}

^{1,1}Dept. Física Fundamental, Universidad Nacional de Educación a Distancia, Aptdo. 60141 E-28080, Madrid, Spain

^{2,2}Courant Institute of Mathematical Sciences, New York University

251 Mercer Street, New York, NY 10012

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We derive a coarse-grained description of the dynamics of a nanoparticle immersed in an isothermal simple fluid by performing a systematic coarse graining of the underlying microscopic dynamics. As coarse-grained or relevant variables we select the position of the nanoparticle and the *total* mass and momentum density field of the fluid, which are locally conserved slow variables because they are defined to include the contribution of the nanoparticle. The theory of coarse graining based on the Zwanzing projection operator leads us to a system of stochastic *ordinary* differential equations (SODEs) that are closed in the relevant variables. We demonstrate that our discrete coarse-grained equations are consistent with a Petrov-Galerkin finite-element discretization of a system of formal stochastic *partial* differential equations (SPDEs) which resemble previously-used phenomenological models based on fluctuating hydrodynamics. Key to this connection between our “bottom-up” and previous “top-down” approaches is the use of the same dual orthogonal set of linear basis functions familiar from finite element methods (FEM), both as a way to coarse-grain the microscopic degrees of freedom, and as a way to discretize the equations of fluctuating hydrodynamics. Another key ingredient is the use of a “linear for spiky” weak approximation which replaces microscopic “fields” with a linear FE interpolant inside expectation values. For the irreversible or dissipative dynamics, we approximate the constrained Green-Kubo expressions for the dissipation coefficients with their equilibrium averages. Under suitable approximations we obtain *closed* approximations of the coarse-grained dynamics in a manner which gives them a clear physical interpretation, and provides *explicit* microscopic expressions for all of the coefficients appearing in the closure. Our work leads to a model for dilute nanocolloidal suspensions that can be simulated effectively using feasibly short molecular dynamics simulations as input to a FEM fluctuating hydrodynamic solver.

I. INTRODUCTION

The study of the Brownian motion of rigid particles suspended in a viscous solvent is one of the oldest subjects in nonequilibrium statistical mechanics since the pioneering work of Einstein [1]. Nevertheless, it was not until the seventies that it was realized how subtle diffusion in liquids is [2–9], and to this day there remain open fundamental questions about the collective diffusion in colloidal suspensions. For example, the validity of Fick’s macroscopic law is questioned for suspensions confined to a two dimensions [10], and it remains as a substantial mathematical challenge to prove that a local Fickian equation is the law of large numbers in three dimensions, even for dilute suspensions [11]. These questions are not of purely academic interest since diffusion is of crucial importance in a number of applications in chemical engineering and materials science, such as the study of the dynamics of passive or active [12, 13] particles in suspension, the dynamics of biomolecules in solution [14, 15], the design of novel nanocolloidal suspensions [16–18], and others. The importance of coarse-graining to the study of diffusion in nanocolloidal suspensions is easy to appreciate; the number of degrees of freedom necessary to simulate Brownian motion directly using Molecular Dynamics (MD) is large enough to make this approach prohibitively expensive. In this paper, we derive from “first principles” a coarse-grained dynamic equation for the po-

sition of a nanoparticle immersed in a simple fluid, fully taking into account hydrodynamic effects.

The key source of difficulty in the theoretical and computational modeling of colloidal diffusion is the presence of viscous dissipation in the surrounding fluid. This hydrodynamic dissipation in the solvent induces long-ranged hydrodynamic fields that couple the motion of the solute particles to boundaries and to other particles. These effects are termed hydrodynamic interactions in the literature, but it should be kept in mind that these “interactions” are different in nature from direct interactions such as steric repulsion or long-ranged attractions among the colloids. The well-known Smoluchowski or Brownian Dynamics (BD) [19, 20] approach captures the effect of the solvent through a mobility matrix that is approximated using hydrodynamic models based on assumptions that are of questionable validity for nanoscopic particles. In particular, a gold nanocolloid and a biomolecule such as a protein can only be distinguished in BD based on an effective hydrodynamic no-slip surface but not based on the nature of their interaction with the solvent. This makes BD unsuitable for capturing multiscale effects such as slip on the surface of the particle, layering of the solvent molecules around the colloid, transient hydrogen bond networks around the protein, etc.

The fluctuation-dissipation balance principle informs us that viscous dissipation is intimately related to fluctu-

ations of the fluid velocity. It is well-known that diffusion in liquids is strongly affected by advection by thermal velocity fluctuations [5, 21–23], and that nonequilibrium diffusive mixing is accompanied by “giant” long-range correlated thermal fluctuations [24–27]. As explained in detail in Refs. [11, 28–30], there is a direct relation between these unusual properties of thermal fluctuations in liquid solutions and Brownian Dynamics. Specifically, a simplified model of colloidal diffusion based on *incompressible fluctuating hydrodynamics* can be mapped one-to-one to the equations of BD and related Dynamic Density Functional Theories (DDFT) with hydrodynamics [31, 32]; this derivation shows that hydrodynamic interactions are nothing more nor less than *hydrodynamic correlations* induced by the thermal fluctuations in the solvent. Such a fluctuating hydrodynamic model [11, 28–30] explains the appearance of giant nonequilibrium fluctuations in the concentration of colloidal particles, justifies the Stokes-Einstein relation in the limit of large Schmidt numbers [33], and describes the important influence of boundaries in confined suspensions [23, 29]. If one wants to further account for inertial effects and compressibility of the fluid, as crucial for modeling the effect of ultrasound on colloidal particles [34] or the acoustic vibrations produced by suspended particles [35] or micro-organisms [36], one can use a similar model but describe the fluid using *compressible* fluctuating hydrodynamics [34, 37, 38].

In this work we consider coupling compressible isothermal fluctuating hydrodynamics to a suspended nanocolloidal particle. Unlike previous phenomenological models [11, 28, 29, 34, 37–42], we obtain our equations from the underlying microscopic dynamics by using the Theory of Coarse-Graining (TCG) as developed by Green [43] and Zwanzig [44] (also see the textbook [45]), together with a sequence of careful approximations that preserve the correct structure of the exact (but formal) coarse-grained equations. Our derivation is important for several reasons. Firstly, our work provides a microscopic foundation for the types of models used in existing theoretical and computational work [11, 28, 29, 34, 37–41]. Secondly, and more importantly, our derivation leads to microscopic Green-Kubo type formulas for the transport coefficients that appear in the coarse-grained equations. This allows for these coefficients to be estimated from molecular dynamics computations, thus fully taking into account microscopic effects that are difficult if not impossible to include in purely continuum models. Thirdly, our derivation will lead us to first construct a microscopically-justified fully discrete form of compressible isothermal fluctuating hydrodynamics that is second-order accurate while also maintaining discrete fluctuation-dissipation balance to second order.

This last contribution is in itself a significant extension of prior work [46], fully consistent with the approach to nonlinear fluctuating hydrodynamics proposed in our recent work [47]. Specifically, the coarse-grained equations we derive here by following a “bottom-up” approach can also be derived by a “top-down” approach in

which one starts from a (phenomenological) system of formal stochastic partial differential equations and applies a Petrov-Galerkin finite-element discretization [47]. Our work therefore provides a direct and *explicit* link between the microscopic discrete dynamics and mesoscopic continuum fluctuating hydrodynamics. The physical insight that is necessary to construct phenomenological fluctuating hydrodynamics equations translates in this paper into physical insight required when constructing suitable approximations or closures of a number of intractable microscopic expressions. The “bottom-up” procedure clearly reveals all of the required terms in the coarse-grained equations and provides microscopic expressions for the required coefficients.

At first sight, it may seem like the equations of Smoluchowski that underlie Brownian dynamics have a well-known microscopic derivation. Indeed, it is not difficult to construct a text-book TCG for the dynamic equation describing the positions of the colloidal particles [48]. This leads to the well-known expression for the hydrodynamic mobility (diffusion tensor) as the time integral of the correlation function of the velocities of the solute particles, conditional on the particle’s positions. It should, however, quickly be recognized that this well-known expression, while correct, is not useful in practice, for several reasons. Firstly, this integral must be computed anew for *every* configuration of the suspended particles. Secondly, even if one could run a new MD calculation at every step in a BD simulation, it is important to realize that these MD computations are *unfeasible* in practice because they must be very long on microscopic scales. Namely, it is well-known that the slow viscous (diffusive) dissipation of momentum in the fluid makes the velocity correlation functions have long (power-law) hydrodynamic tails; it is the integral of these tails that gives the hydrodynamic correlations (interactions) among the particles, as well as finite-size effects on the diffusion coefficient for confined particles [22]. Therefore, to correctly capture hydrodynamic effects the time integral in the Green-Kubo expression for the diffusion tensor must extend to at least the time it takes for momentum to diffuse throughout the *whole* system; while this time is typically short compared to the time scale at which the solute particles move, it is very long based on MD standards.

By contrast, in the equations derived here the Green-Kubo integrals can be computed via *feasible* (short) MD simulations. This is because all of the hydrodynamics, such as the effects of sound [34] or viscous dissipation [38] are captured by explicitly resolving the (fluctuating) hydrodynamics of the solvent using a grid of hydrodynamic cells, and only the remaining *local* and *short-time* effects need to be captured by the microscopic simulations. In the present work, we consider suspensions that are sufficiently dilute to allow us to neglect the direct (as opposed to hydrodynamic) interactions among the colloids and focus our derivation on a single particle immersed in a viscous liquid; hydrodynamic interactions

among the particles are still captured because they are mediated by the explicitly resolved surrounding fluid dynamics. In fact, we believe that in many cases of interest the coarse-grained diffusive dynamics can effectively be simulated by *a priori* performing a small number of short MD simulations of a single particle in a small (say periodic) domain. Crucial to the above is the fact that in the present work the hydrodynamic cells are assumed to be significantly larger than the nanoparticle itself.

In the next section we explain in more detail the basic assumptions and thus limitations of our model. Briefly, our model assumes that the solvent is a simple isotropic single-component fluid. We do not explicitly consider energy transport and thus limit our work to isothermal suspensions. We only consider dilute suspensions of nanoparticles. The extension to denser suspension leads to a significantly more complicated theory of liquid mixtures that is well beyond the scope of this work. The limitation to nanoscopic particles is not essential and the equations developed here can be used also for larger particles such as micron-sized colloids; however, in this case the MD simulations required to obtain the values of the Green-Kubo integrals that appear in the coarse-grained equations would again become unfeasible and a different approach is advised. We will also assume that the particle is effectively spherical so that describing the position of its center of mass is sufficient without requiring us to also resolve its orientation. Our theory assumes a separation of time scales between the positions of the particles and their velocities, and we do not include the velocities of the colloidal particles in the description. More precisely, it requires that the Schmidt number of the solute particles be very large. This is not a significant limitation in practice since the Schmidt number of even a single solvent molecule is typically very large in liquids. In particular, our theory can be used to describe collective diffusion of tagged solvent particles (i.e., self-diffusion).

In Section II we explain the basic notation and concepts, and carefully select and define the coarse-grained (slow) variables in terms of the microscopic degrees of freedom. We then proceed to carefully examine the reversible (non-dissipative) part of the dynamics. In particular, in Section III A we give exact results that are not useful on their own right since they lead to equations that are not closed explicitly. However, by making a series of approximations based on a key “linear for spiky” approximation we are able to derive an approximate closure for the reversible dynamics in Section III B. In Section IV we apply the same approximation to the irreversible (dissipative) part of the dynamics, together with another important approximation in which we replace constrained Green-Kubo expressions with unconstrained equilibrium Green-Kubo averages. The key results of our calculations are then collected and discussed in Section V. We first give an approximate but *closed* form for the coarse-grained *discrete* dynamics, and then discuss the relation of these discrete equations to continuum models in Section V C. A comparison of our results to phenomenologi-

cal models and a discussion of their significance and range of validity is given in Section VI. A number of technical calculations are detailed in an extensive Appendix.

II. COARSE-GRAINING

In this section, we give the basic ingredients required to perform the coarse-graining of the microscopic dynamics for our specific system. We begin with a general overview of the theory and then specialize to the case of a nanoparticle suspended in a simple liquid by explaining the details of the microscopic dynamics and the definition of the coarse-grained variables.

A. The Theory of Coarse-Graining

In this section, we review the theory of Coarse-Graining or Non-Equilibrium Statistical Mechanics as established by Green [43] and Zwanzig [44]. The theory allows to construct the dynamic equations for the probability distribution of a set of coarse-grained (CG) variables that describe the state of a system at a coarse *level of description*. The theory states that, under the assumption that the CG variables are sufficiently slow as compared with the eliminated degrees of freedom, the system follows a diffusion process in the space of CG variables. The resulting dynamic equation for the probability distribution of the CG variables is given by a Fokker-Planck equation (FPE), where both the drift and diffusion terms are given in microscopic terms.

The coarse-grained variables are selected functions $\hat{x}(z)$ in phase space, i.e. they depend on the set of position and momenta z of the molecules of the system. We follow the convention that a hatted symbol like $\hat{x}(z)$ denotes a function in phase space that may take numerical values x . The selection of the relevant variables $\hat{x}(z)$ is a crucial step in the description of a non-equilibrium system. A crucial requirement is that they are *slow* variables [49]. When this is the case, the probability distribution of a set of relevant variables x obeys the FPE

$$\begin{aligned} \partial_t P(x, t) = & -\frac{\partial}{\partial x} \cdot \left\{ \left[\mathcal{A}(x) - \mathcal{D}(x) \cdot \frac{\partial \mathcal{H}}{\partial x}(x) \right] P(x, t) \right\} \\ & + k_B T \frac{\partial}{\partial x} \cdot \left\{ \mathcal{D}(x) \cdot \frac{\partial}{\partial x} P(x, t) \right\} \end{aligned} \quad (1)$$

The different objects in this equation have a well-defined microscopic definition. For example, the *reversible drift* is

$$\mathcal{A}(x) = \langle L \hat{x} \rangle^x \quad (2)$$

where L is the Liouville operator and the conditional ex-

pectation is defined by

$$\langle \dots \rangle^x = \frac{1}{P^{\text{eq}}(x)} \int dz \rho^{\text{eq}}(z) \delta(\hat{x}(z) - x) \dots \quad (3)$$

where $\rho^{\text{eq}}(z)$ stands for the microscopic equilibrium distribution and $\delta(\hat{x}(z) - x)$ is actually a product of Dirac delta functions, one for every function $\hat{x}(z)$. The equilibrium distribution of the relevant variables is

$$P^{\text{eq}}(x) = \int dz \rho^{\text{eq}}(z) \delta(\hat{x}(z) - x) \quad (4)$$

and is closely related to the *bare free energy* of the level of description x which is defined through

$$\mathcal{H}(x) \equiv -k_B T \ln P^{\text{eq}}(x) \quad (5)$$

Here k_B is Boltzmann's constant and T the temperature of the equilibrium state. We will refer in this work to the bare free energy also as the coarse-grained Hamiltonian because of the particular form that $\mathcal{H}(x)$ acquires at the hydrodynamic level of description. When non-isothermal situations are considered one rather introduces the entropy of the level of description as $\mathcal{S}(x) = k_B \ln P^{\text{eq}}(x)$, according to Einstein formula for fluctuations.

Finally, the symmetric and positive semidefinite [45] *dissipative matrix* $\mathcal{D}(x)$ is the matrix of transport coefficients expressed in the form of Green-Kubo formulas,

$$\mathcal{D}(x) = \frac{1}{k_B T} \int_0^\infty \langle Q L \hat{X} \exp\{i Q L t'\} Q L \hat{X} \rangle^x dt' \quad (6)$$

The term $Q L \hat{X}$ is the so called *projected current*. The projection operator Q is defined from its action on any phase function $\hat{B}(z)$ [44]

$$Q \hat{B}(z) = \hat{B}(z) - \langle \hat{B} \rangle^{\hat{x}(z)} \quad (7)$$

The dynamic operator $\exp\{i Q L t'\}$ is usually named the projected dynamics, which is, strictly speaking different from the real Hamiltonian dynamics $\exp\{L t'\}$. The projected dynamics can be usually approximated by the real dynamics but, in order to avoid the so called *plateau problem* [49], then the upper infinite limit of integration in Eq. (6) has to be replaced by τ , a time which is long in front of the correlation time of the integrand, but short in front of the time scale of evolution of the macroscopic variables [45, 49–51], this is

$$\mathcal{D}(x) = \frac{1}{k_B T} \int_0^\tau \langle Q L \hat{X} \exp\{i L t'\} Q L \hat{X} \rangle^x dt' \quad (8)$$

In general, it is expected that different elements of the matrix may require different values of τ .

The Ito stochastic differential equation (SDE) that is mathematically equivalent to the FPE (1) is given by

$$\frac{dx}{dt} = \mathcal{A}(x) - \mathcal{D}(x) \cdot \frac{\partial \mathcal{H}}{\partial x}(x) + k_B T \frac{\partial}{\partial x} \cdot \mathcal{D}(x) + \frac{d\tilde{x}}{dt}(x) \quad (9)$$

where $\frac{d\tilde{x}}{dt}(x) = B(x) \frac{d\mathcal{B}(t)}{dt}$ is a linear combination of white noises, formally time derivatives of a collection of independent Wiener processes (Brownian motions) $\mathcal{B}(t)$, where the amplitudes satisfy the Fluctuation-Dissipation Balance (FDB) condition

$$B(x)^T B(x) = 2k_B T \mathcal{D}(x) \quad (10)$$

In summary, the three basic objects that determine the dynamics (either in the FPE (1) or the SDE (9) forms) and that need to be computed in the theory are the bare free energy $\mathcal{H}(x)$, the reversible drift $\mathcal{A}(x)$, and the dissipative matrix $\mathcal{D}(x)$.

The reversible drift can also be written in the form [45]

$$\mathcal{A}_\mu(x) = L_{\mu\nu}(x) \frac{\partial \mathcal{H}}{\partial x_\nu}(x) - k_B T \frac{\partial L_{\mu\nu}}{\partial x_\nu}(x) \quad (11)$$

where the skew-symmetric reversible matrix is defined as

$$L_{\mu\nu}(x) = \langle \{X_\mu, X_\nu\} \rangle^x \quad (12)$$

where $\{\cdot, \cdot\}$ is the Poisson bracket. Here and in what follows, Einstein convention that sums over repeated indices is assumed. Note that the form of the drift (11) ensures automatically the Gibbs-Boltzmann distribution $P^{\text{eq}}(x) \propto e^{-\beta \mathcal{H}(x)}$ is the equilibrium solution of (1), *even for approximate forms* of the reversible matrix $L(x)$ and the CG Hamiltonian $\mathcal{H}(x)$, and, thus, is the preferred form for the reversible drift in the present work.

B. Selection of Coarse-Grained Variables

The most important step in the TCG is the selection of the *relevant* (coarse-grained) *variables*. This selection must be guided by physical intuition and the presence or absence of separation of time scales. The key guiding principle is that the relevant variables must evolve much more slowly than *all* other variables that cannot be expressed entirely in terms of the relevant variables. This allows us to make a Markovian approximation of the coarse-grained dynamics, which takes the form of a Fokker-Planck equation for the probability distribution of relevant variables, or equivalently, of a stochastic differential equation for the instantaneous (fluctuating) relevant variables.

Ultimately, one is often only interested in the positions (and possibly orientations) of the colloidal particles, eliminating the solvent from consideration entirely. This is possible to do via TCG because indeed in liquids mass diffusion is very slow compared to momentum and heat diffusion, and thus the positions of the particles are much slower than the hydrodynamic fields. Indeed, following the TCG using only the positions of the particles leads to the well known equations of Smoluchowski or Brownian dynamics, with well-known Green-Kubo expressions for the hydrodynamic mobility (equivalently, diffusion) matrix (see, for example, Section V in [48]). As we ex-

plained above, this level of description is not sufficiently detailed to allow us to describe a number of important microscopic effects that occur in the vicinity of the particle surface. While in the present work we do not capture explicitly the slip at the surface and the layering effects around a nanoparticle, we do take into account such effects implicitly through the microscopic expressions that enter in the theory. Furthermore, the Green-Kubo formulas for the mobility are not useful in practice and one must close the equations by using a pairwise approximation to the mobility matrix based on far-field expansions for Stokes flow.

To go to a more fundamental (microscopically more informed) level of description we must include solvent degrees of freedom as well. We want to describe the solvent molecules at the hydrodynamic rather than the microscopic level since it is not reasonable to keep track of the positions and momenta of every molecule in the system. At macroscopic scales, a fluid appears as a continuum that is described with smooth fields obeying the well-known Navier-Stokes equations. The “field” concept is tricky, though, because a field is a mathematical object that has infinitely many degrees of freedom, while the actual fluid system has a finite number of degrees of freedom. Of course, the fields are defined above a certain spatial resolution much larger than the typical size and distances between molecules of the fluid. At these macroscopic scales the field at one point of space effectively represents a very large number of molecules that move in a coherent manner. When one descends down to mesoscopic scales, molecules do not move that coherently, and one starts appreciating the discrete nature of the fluid. In other words, the average behavior and the actual behavior of the fluid molecules start to differ, and it is necessary to describe a fluid system with hydrodynamic equations that are intrinsically stochastic. The first phenomenological theory for such fluctuating hydrodynamics was proposed by Landau and Lifshitz, who introduced the concepts of random stress and heat fluxes, to be added to the usual Newtonian stress and Fourier heat flux [52].

From a mathematical point of view, the nonlinear stochastic partial differential equations (SPDEs) of fluctuating hydrodynamics are ill-defined. In other words, a continuum limit of sequences of more refined otherwise reasonable discrete versions of the partial differential equation does not exist. From a physical point of view, though, this is not much of a problem because we know that the continuum limit cannot be realized without first encountering the atomistic nature of matter. For these reasons, it is necessary to define *discrete* hydrodynamic variables by averaging over a number of nearby molecules, and use these discrete variables in the TCG. In this work, following the approach developed in a sequence of prior works [46, 47, 53], we define discrete hydrodynamic fields by placing a fixed (Eulerian) grid of hydrodynamic *nodes* and associating to each node a fluid density and momentum averaged over a hydrody-

namic *cell* associated to that node. In the present work we compute with more rigor some of the conditional expectations that were plausibly approximated in [46]. In order to have a reasonable hydrodynamics description we need to have hydrodynamic cells that contain many solvent molecules; here we consider simple liquids for which hydrodynamic cells containing many molecules will also be much larger than the mean free path.

For a colloidal particle that is much larger than the solvent molecules, the hydrodynamic flow around the nanoparticle can be resolved with small (compared to the size of the nanoparticle) hydrodynamic cells that, nevertheless, still contain many solvent molecules. In this situation, the discrete *fluid* mass density ρ_μ , and the discrete *fluid* momentum densities \mathbf{g}_μ , where μ indexes the hydrodynamic nodes, would only include contributions from the solvent particles. At such a level of description it is necessary to include both the position \mathbf{R} and the momentum \mathbf{P} of the nanoparticle in the list of relevant variables because even though \mathbf{P} is much faster than the position, it evolves on the same time scale as the hydrodynamic momentum around the particle. This level of description has been traditionally used for the description of Brownian motion of colloidal particles coupled with fluctuating hydrodynamics [2, 3]. We do not consider this case here; for a phenomenological model of this type we refer the reader to Refs. [34, 37, 38]. It is important to note that it is inconsistent to keep the velocities and thus inertial dynamics of the particles without also accounting for the viscosity and inertia of the surrounding fluid. This is because there is not a separation of time scales between the velocities of the particles and the velocity of the surrounding fluid; the *only* consistent coarse-grained *implicit-fluid* level of description is that of Brownian dynamics, as explained in detail by Roux [9].

Here we consider a nanoparticle that is not much larger than the fluid molecules, so that the hydrodynamic cells are much larger than the nanocolloidal particle, i.e., we have a “subgrid” colloidal particle. In particular, the “nanoparticle” particle could be just a tagged fluid molecule when modeling self-diffusion in a liquid. Since the momentum of the particle evolves on the same time scale as the solvent molecules with which it collides, more precisely, since the fluctuations of the *relative* velocity of the colloid are fast compared to hydrodynamic time scales, we define the hydrodynamic mass and momentum density fields to *include the nanoparticle contribution*. In summary, the level of description that we consider in this work is characterized by the position of the colloid \mathbf{R} , the (total, i.e., including the contribution from the nanoparticle) discrete mass density ρ_μ , and the (total) discrete momentum density \mathbf{g}_μ , where μ indexes the hydrodynamic nodes.

We make use of the standard TCG of Zwanzig where all the terms (CG free energy, drift, and diffusion matrix) are given in microscopic terms [44, 45]. This allows one to obtain the general structure of the dynamics. However in order to find tractable results it is crucial to make a

number of assumptions. All the approximations that we consider rely on the fact that the cells used to define the hydrodynamic variables are much larger than the typical intermolecular distances in such a way that every cell contains many molecules of the fluid. In particular, we assume that the microscopic local density field which is of the form $\sum_i^N m_i \delta(\mathbf{r} - \mathbf{q}_i)$ gives, once inside conditional expectations, the same result as the interpolated discrete density variables (see Eq. (49) below and Fig. 3). This is only plausible if, again, there are many molecules per cell and the values of the discrete variables in neighboring cells are very similar. While this is a statement about the flow regimes for which the resulting equations apply, it is also a statement about the size of the fluctuation of the hydrodynamic variables. They need to be *small*, otherwise, the value in neighbor cells could be very different just by chance. In other words, the number of molecules per cell must be sufficiently large in order for the relative fluctuations to be sufficiently small. In the end, the validity of the approximations made and the utility of the final equations we obtain can only be judged by a computational comparison to the true microscopic dynamics (molecular dynamics).

C. Microscopic Dynamics

In the present work we consider a simple liquid system of $N + 1$ particles described with the position and momenta of their center of mass (see Fig. 1 for a schematic representation), in a periodic box. We distinguish particle $i = 0$ as the nanoparticle which has a mass m_0 , typically larger than the mass m of a solvent particle. At the *microscopic level* the system is described by the set z of all positions \mathbf{q}_i and momenta $\mathbf{p}_i = m_i \mathbf{v}_i$ ($i = 0, 1, \dots, N$) of the particles. The microstate of the system evolves according to Hamilton's equations with Hamiltonian given by

$$\begin{aligned} \hat{H}(z) &= \frac{\mathbf{p}_0^2}{2m_0} + \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \hat{U}(q) \\ \hat{U}(q) &= \hat{U}^{\text{sol}}(q) + \sum_{i=1}^N \Phi^{\text{int}}(q_{0i}) + \Phi^{\text{ext}}(\mathbf{q}_0) \\ \hat{U}^{\text{sol}}(q) &= \frac{1}{2} \sum_{i,j=1}^N \phi(q_{ij}) \end{aligned} \quad (13)$$

We have assumed a pairwise potential energy $\phi(q_{ij})$ between liquid molecules i, j separated a distance q_{ij} . $\hat{U}^{\text{sol}}(q)$ is the potential energy of the solvent in the absence of the nanoparticle, $\Phi^{\text{int}}(q)$ is the potential of interaction of the i -th solvent particle with a nanoparticle a distance q away, and $\Phi^{\text{ext}}(\mathbf{q}_0)$ is an external time-independent potential acting on the nanoparticle. The system is assumed to have periodic boundary conditions.

Under the assumption that the Hamiltonian is mixing,

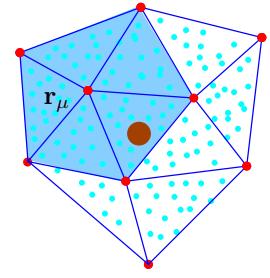


FIG. 1: Schematic representation of a nanoparticle (in brown) surrounded by molecules of a simple liquid solvent (in blue). Also shown is the triangulation that allows to define the discrete hydrodynamic variables at the nodes (in red). The shaded area around node μ located at \mathbf{r}_μ is the support of the finite element function $\psi_\mu(\mathbf{r})$ and defines the hydrodynamic cell.

the dynamics will sample at long times the *molecular ensemble* [54] given by

$$\rho^{\text{eq}}(z) = \frac{1}{\Omega(E_0, \mathbf{P}_0)} \delta \left(\sum_{i=0} \mathbf{p}_i - \mathbf{P}_0 \right) \delta (H(z) - E_0) \quad (14)$$

where \mathbf{P}_0 and E_0 are the initial total momentum and energy of the system. We will assume that in the thermodynamic limit the molecular ensemble can be approximated by the canonical ensemble

$$\rho^{\text{eq}}(z) = \frac{1}{Z} \exp\{-\beta \hat{H}(z)\}, \quad (15)$$

where $\beta = 1/(k_B T)$, and we use the canonical ensemble in the theory for simplicity.

D. Definition of Coarse-Grained Variables

The first step in the Theory of Coarse-Graining is to specify the relevant variables in terms of the microscopic state z of the system. In the present case, we choose as relevant variables the position of the nanoparticle

$$\hat{\mathbf{R}}(z) = \mathbf{q}_0, \quad (16)$$

and the mass and momentum hydrodynamic “fields”. As we will consider fluctuations in the hydrodynamic variables, the latter need to be defined in discrete terms [47]. This is, we want to look at the mass and momentum of collections of molecules that are in a given region of space. To this end, we seed physical space with a set of M nodes, located at the points \mathbf{r}_μ . Usually, the nodes are arranged in a regular lattice, but this is not necessary in what follows and arbitrary simplicial grids can be used (see Fig. 1 for a schematic representation).

We define the mass and momentum densities of the

node μ according to

$$\begin{aligned}\hat{\rho}_\mu(z) &= \sum_{i=0}^N m_i \delta_\mu(\mathbf{q}_i) \\ \hat{\mathbf{g}}_\mu(z) &= \sum_{i=0}^N \mathbf{p}_i \delta_\mu(\mathbf{q}_i)\end{aligned}\quad (17)$$

where the index $i = 0$ labels the nanoparticle. The basis function $\delta_\mu(\mathbf{r})$ is a function (with dimensions of inverse of a volume) that is appreciably different from zero only in the vicinity of \mathbf{r}_μ . This region is referred to as the hydrodynamic cell of node μ . We may regard the basis function $\delta_\mu(\mathbf{r})$ as a “discrete Dirac delta function”. Its specific form is discussed below. Note that both the mass and momentum densities contain the nanoparticle in their definition. It is convenient to introduce also the hydrodynamic fields of the solvent

$$\begin{aligned}\hat{\rho}_\mu^{\text{sol}}(z) &= \sum_{i=1}^N m_i \delta_\mu(\mathbf{q}_i) \\ \hat{\mathbf{g}}_\mu^{\text{sol}}(z) &= \sum_{i=1}^N \mathbf{p}_i \delta_\mu(\mathbf{q}_i)\end{aligned}\quad (18)$$

that do not contain in its definition the contribution of the nanoparticle (i.e. the particle $i = 0$ is excluded in the sum).

We may express the discrete hydrodynamic variables (17) and (18) in terms of the usual microscopic densities

$$\begin{aligned}\hat{\rho}_{\mathbf{r}}(z) &= \sum_{i=0}^N m_i \delta(\mathbf{r} - \mathbf{q}_i), & \hat{\rho}_{\mathbf{r}}^{\text{sol}}(z) &= \sum_{i=1}^N m_i \delta(\mathbf{r} - \mathbf{q}_i) \\ \hat{\mathbf{g}}_{\mathbf{r}}(z) &= \sum_{i=0}^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i), & \hat{\mathbf{g}}_{\mathbf{r}}^{\text{sol}}(z) &= \sum_{i=1}^N \mathbf{p}_i \delta(\mathbf{r} - \mathbf{q}_i)\end{aligned}\quad (19)$$

as simple space integrals,

$$\begin{aligned}\hat{\rho}_\mu(z) &= \int d\mathbf{r} \delta_\mu(\mathbf{r}) \hat{\rho}_{\mathbf{r}}(z), & \hat{\rho}_\mu^{\text{sol}}(z) &= \int d\mathbf{r} \delta_\mu(\mathbf{r}) \hat{\rho}_{\mathbf{r}}^{\text{sol}}(z) \\ \hat{\mathbf{g}}_\mu(z) &= \int d\mathbf{r} \delta_\mu(\mathbf{r}) \hat{\mathbf{g}}_{\mathbf{r}}(z), & \hat{\mathbf{g}}_\mu^{\text{sol}}(z) &= \int d\mathbf{r} \delta_\mu(\mathbf{r}) \hat{\mathbf{g}}_{\mathbf{r}}^{\text{sol}}(z)\end{aligned}\quad (20)$$

Note that the two sets of variables $\{\hat{\mathbf{R}}, \hat{\rho}, \hat{\mathbf{g}}\}$ and $\{\hat{\mathbf{R}}, \hat{\rho}^{\text{sol}}, \hat{\mathbf{g}}^{\text{sol}}\}$ are not expressible in terms of each other. While we have that the densities are related as

$$\hat{\rho}_\mu^{\text{sol}}(z) = \hat{\rho}_\mu(z) - m_0 \delta_\mu(\hat{\mathbf{R}}) \quad (21)$$

there is no way to express the momentum $\hat{\mathbf{g}}$ as a function of $\mathbf{R}, \hat{\rho}^{\text{sol}}, \hat{\mathbf{g}}^{\text{sol}}$. Therefore, the dynamic equations to be obtained for each set of variables are *essentially different* and cannot be obtained from each other through a simple change of variables. In other words, the two sets of rel-

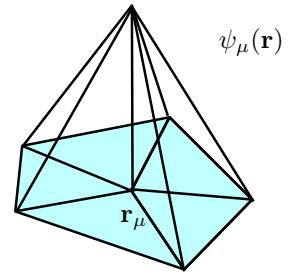


FIG. 2: The finite element basis function $\psi_\mu(\mathbf{r})$ in two dimensions.

evant variables lead to *physically different* descriptions. Since the slowness of the hydrodynamic variables arises from the underlying conservation laws, and only the *total* mass and momentum fields are conserved quantities, the appropriate variables for the TCG are our chosen variables $\{\hat{\mathbf{R}}, \hat{\rho}, \hat{\mathbf{g}}\}$.

E. The basis functions

The actual form of the discrete Dirac delta function $\delta_\mu(\mathbf{r})$ needs to be specified. One possibility is to use the characteristic function (divided by the volume of the cell) of the Voronoi cell of node μ . For $\hat{\rho}_\mu(z)$ this will give the total mass (per unit volume) of the particles that happen to be within the Voronoi cell μ . As we discussed in Ref. [55], though, this selection is unsuited for the derivation of the equations governing discrete hydrodynamics from the Theory of Coarse-Graining. This is because the gradient of the characteristic function of the Voronoi cell is singular and leads to ill-defined Green-Kubo expressions. It was suggested to instead use the Delaunay triangulation associated with the set of nodes as a grid of finite elements (FE), and take the discrete delta function to be the linear FE basis function $\psi_\mu(\mathbf{r})$ associated with node μ , which has the characteristic shape of a tent in one dimension, a pyramid in two dimensions (as shown in Fig. 2), and more generally a $(d+1)$ -dimensional simplex in d dimensions. Note that the use of a Voronoi/Delaunay tessellation is not required, and any simplicial grid (i.e., a triangular grid in two dimensions or a tetrahedral grid in three dimensions) whose vertices are the set of hydrodynamic nodes can be used equally well (but for numerical purposes the grid should be kept as close to uniform as possible).

In recent work [47, 56], we have argued that an even better selection (in terms of numerical accuracy) is given by a basis function $\delta_\mu(\mathbf{r})$ that is a linear combination of the (dimensionless) finite element linear basis functions functions $\psi_\mu(\mathbf{r})$

$$\delta_\mu(\mathbf{r}) = M_{\mu\nu}^\delta \psi_\nu(\mathbf{r}), \quad (22)$$

The crucial requirement is that these basis functions are

mutually orthogonal

$$\|\delta_\mu \psi_\nu\| = \delta_{\mu\nu} \quad (23)$$

where we have introduced double bars to denote integration over space, this is

$$\|f\| \equiv \int d\mathbf{r} f(\mathbf{r}) \quad (24)$$

for an arbitrary function $f(\mathbf{r})$. Note that from (22) and (23) it follows the explicit matrix form

$$M_{\mu\nu}^\delta = \|\delta_\mu \delta_\nu\| \quad (25)$$

If we introduce the usual ‘‘mass matrix’’ of the finite element method

$$M_{\mu\nu}^\psi = \|\psi_\mu \psi_\nu\| \quad (26)$$

the orthogonality condition implies that $M_{\mu\nu}^\delta$ in (22) is given by the inverse of $M_{\mu\nu}^\psi$, this is

$$M_{\mu\nu}^\psi M_{\nu\sigma}^\delta = \delta_{\mu\sigma} \quad (27)$$

The basis function $\delta_\mu(\mathbf{r})$ may be regarded as a way of discretizing a field $a(\mathbf{r})$ according to $a_\mu = \|\delta_\mu a\|$. The basis function $\psi_\mu(\mathbf{r})$ permits to construct interpolated fields out of the discrete fields $\bar{a}(\mathbf{r}) = \sum_\mu a_\mu \psi_\mu(\mathbf{r})$. The orthogonality condition (23) ensures that if we discretize an interpolated field, we recover the original discrete values, i.e. $\|\delta_\mu \bar{a}\| = a_\mu$. This is the main motivation to use the slightly more involved basis function $\delta_\mu(\mathbf{r})$ instead of the finite element $\psi_\mu(\mathbf{r})$ for the definition of the CG variables. It turns out that this complication pays off, as the resulting finite difference operators are second order accurate approximations of the corresponding continuum differential operator, even in irregular grids [56].

The finite element linear basis functions satisfy a partition of unity and give linear consistency,

$$\sum_\mu \psi_\mu(\mathbf{r}) = 1, \quad \sum_\mu \mathbf{r}_\mu \psi_\mu(\mathbf{r}) = \mathbf{r} \quad (28)$$

As a consequence of these properties, the conjugate basis functions $\delta_\mu(\mathbf{r})$ satisfy

$$\sum_\mu \mathcal{V}_\mu \delta_\mu(\mathbf{r}) = 1, \quad \sum_\mu \mathcal{V}_\mu \mathbf{r}_\mu \delta_\mu(\mathbf{r}) = \mathbf{r} \quad (29)$$

where \mathcal{V}_μ is the volume of the hydrodynamic cell μ

$$\mathcal{V}_\mu \equiv \int d\mathbf{r} \psi_\mu(\mathbf{r}) \quad (30)$$

Note that we have

$$\int d\mathbf{r} \delta_\mu(\mathbf{r}) = 1, \quad \int d\mathbf{r} \mathbf{r} \delta_\mu(\mathbf{r}) = \mathbf{r}_\mu \quad (31)$$

as can be proved by using (28) and the orthogonality (23). These properties justify to call $\delta_\mu(\mathbf{r})$ a discrete Dirac delta function.

The partition of unity reflected in (29) implies

$$\sum_\mu \mathcal{V}_\mu \nabla \delta_\mu(\mathbf{r}) = 0 \quad (32)$$

which we will use often in proving that the resulting dynamic equations are conservative. In fact, we define the total mass and total momentum of the system at the CG level through,

$$\begin{aligned} M_T &\equiv \sum_\mu \mathcal{V}_\mu \hat{\rho}_\mu(z) = \sum_i m_i \\ \mathbf{P}_T &\equiv \sum_\mu \mathcal{V}_\mu \hat{\mathbf{g}}_\mu(z) = \sum_i \mathbf{p}_i \end{aligned} \quad (33)$$

which are, indeed, the total mass and momentum. These quantities are conserved by the microscopic dynamics and need to be conserved by the coarse-grained dynamics.

It is convenient to introduce also the following *regularized* Dirac delta function

$$\Delta(\mathbf{r}, \mathbf{r}') \equiv \delta_\mu(\mathbf{r}) \psi_\mu(\mathbf{r}') = \Delta(\mathbf{r}', \mathbf{r}), \quad (34)$$

which is closely related to what is called the discrete Delta function or interpolation kernel in [29, 34, 37–41]. This function is different from zero only for distances of the order of the size of the hydrodynamic cells. In the limit of zero lattice spacing $\Delta(\mathbf{r}, \mathbf{r}')$ converges in weak sense to $\delta(\mathbf{r} - \mathbf{r}')$. Therefore, $\Delta(\mathbf{r}, \mathbf{r}')$ can be understood as a Dirac delta function regularized on the scale of the grid.

The regularized Dirac delta satisfies the exact identities

$$\begin{aligned} \int d\mathbf{r}' \Delta(\mathbf{r}, \mathbf{r}') \delta_\mu(\mathbf{r}') &= \delta_\mu(\mathbf{r}) \\ \int d\mathbf{r}' \Delta(\mathbf{r}, \mathbf{r}') \psi_\mu(\mathbf{r}') &= \psi_\mu(\mathbf{r}) \end{aligned} \quad (35)$$

One of the basic approximations that we will make in the present work is the *smoothness approximation*

$$\int d\mathbf{r}' A(\mathbf{r}') \Delta(\mathbf{r}', \mathbf{r}) = \|A \delta_\mu\| \psi_\mu(\mathbf{r}) \simeq A(\mathbf{r}) \quad (36)$$

for a smooth function $A(\mathbf{r})$. For smooth functions the regularized Dirac delta acts like a Dirac delta. The approximation (36) is an *exact* identity for linear functions $A(\mathbf{r}) = a + \mathbf{r} \cdot \mathbf{b}$. Therefore, the errors committed when using the approximation (36) for smooth functions *are of second order in the lattice spacing*. Sometimes, we will use the above identity in the form

$$\|A \delta_\mu\| \| \psi_\mu B \| \simeq \|AB\| \quad (37)$$

for any two smooth functions $A(\mathbf{r}), B(\mathbf{r})$.

Finally, note that one property that is *not* satisfied by the regularized Dirac delta function, as opposed to the Dirac delta is the following symmetry

$$\frac{\partial}{\partial \mathbf{r}} \Delta(\mathbf{r}, \mathbf{r}') = -\frac{\partial}{\partial \mathbf{r}'} \Delta(\mathbf{r}, \mathbf{r}') \quad (38)$$

If the regularized Dirac delta function was translationally invariant, i.e. $\Delta(\mathbf{r}, \mathbf{r}') = \Delta(\mathbf{r} - \mathbf{r}')$, this would be obviously true. In this case, we would have in addition to (35) also the following relations,

$$\begin{aligned} \int d\mathbf{r}' \Delta(\mathbf{r}, \mathbf{r}') \nabla' \delta_\mu(\mathbf{r}') &= \nabla \delta_\mu(\mathbf{r}) \\ \int d\mathbf{r}' \Delta(\mathbf{r}, \mathbf{r}') \nabla' \psi_\mu(\mathbf{r}') &= \nabla \psi_\mu(\mathbf{r}) \end{aligned} \quad (39)$$

Even though these identities are not fulfilled, we will assume that they are reasonable approximations, particularly if both sides are multiplied with “smooth discrete fields”, i.e.

$$\int d\mathbf{r}' \Delta(\mathbf{r}, \mathbf{r}') \nabla' \bar{a}(\mathbf{r}') \simeq \nabla \bar{a}(\mathbf{r}) \quad (40)$$

For a sufficiently smooth field $\bar{a}(\mathbf{r})$, the length scale of variation of $\nabla \bar{a}(\mathbf{r})$ is much larger than the length scale of variation of $\Delta(\mathbf{r}, \mathbf{r}')$ and, therefore, $\Delta(\mathbf{r}, \mathbf{r}')$ acts as an ordinary Dirac delta.

F. Notation

The notation in the present work is unavoidably dense because many different mathematical objects need to be carefully distinguished. Below we present a summary of the notation for the case of the mass density variable alone. Similar symbols are used for the velocity and momentum density variables. In general, hatted symbol like in

$$\hat{\rho}_\mu(z) = \sum_{i=0}^N m_i \delta_\mu(\mathbf{q}_i), \quad \hat{\rho}_{\mathbf{r}}(z) = \sum_{i=0}^N m_i \delta(\mathbf{q}_i - \mathbf{r}), \quad (41)$$

denote phase functions. The numerical values taken by a phase function are denoted without hat as in, for example, ρ_μ . The subscript is used here to distinguish the specific node μ for discrete variables such as $\hat{\rho}_\mu$, or the specific point in space for continuum fields such as $\hat{\rho}_{\mathbf{r}}$. Overlined symbols like

$$\bar{\rho}(\mathbf{r}) = \psi_\mu(\mathbf{r}) \rho_\mu \quad (42)$$

denote continuum fields which are interpolated from discrete “fields”. Differential operators act only on the symbol immediately to their left unless otherwise indicated by parenthesis, dot denotes contraction, and colon a double contraction.

III. THE REVERSIBLE DRIFT

In this section, we present a number of exact and then approximate results for the reversible part $\mathcal{A}(x)$ of the dynamics and the bare free energy $\mathcal{H}(x)$ for the present level of description.

The exact results presented in section III A are obtained by integrating the microscopic momenta in the microscopic definitions (2) and (4) for these quantities. This integration is possible because we assume that the equilibrium ensemble is given by the canonical ensemble (15) and the resulting space integrals involve relatively simple Gaussian integrals of the kind discussed in Appendix E. The molecular ensemble (14) can also be used at the expense of much cumbersome expressions. We assume that in the thermodynamic limit both ensembles are equivalent and we opt for the simpler case. In Section III B we approximate the exact results in order to obtain a closed form of the reversible drift. In the present section we simply quote the exact results and redirect to the appendices for the specific calculations.

A. The exact reversible drift

We have obtained in Eq. (A24) of Appendix A the following exact form for the reversible drift $\mathcal{A}(x)$ in the form (11) with the evidently skew-symmetric reversible generator

$$L = \begin{pmatrix} 0 & 0 & \delta_\mu(\mathbf{R}) \\ 0 & 0 & \llbracket \hat{\rho} \delta_\nu \nabla^\beta \delta_\mu \rrbracket^{\mathbf{R} \rho \mathbf{g}} \\ -\delta_\mu(\mathbf{R}) & -\llbracket \hat{\rho} \delta_\mu \nabla^\alpha \delta_\nu \rrbracket^{\mathbf{R} \rho \mathbf{g}} & \llbracket \hat{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu \rrbracket^{\mathbf{R} \rho \mathbf{g}} - \llbracket \hat{\mathbf{g}}^\beta \delta_\mu \nabla^\alpha \delta_\nu \rrbracket^{\mathbf{R} \rho \mathbf{g}} \end{pmatrix} \quad (43)$$

The double square brackets act on arbitrary space-dependent phase functions $\hat{f}_{\mathbf{r}}(z)$ and denote the double

operation of conditional averaging and space integration,

this is

$$[\hat{f}]^{\mathbf{R}\rho\mathbf{g}} \equiv \int d\mathbf{r} \left\langle \hat{f}_{\mathbf{r}} \right\rangle^{\mathbf{R}\rho\mathbf{g}} \quad (44)$$

where $\langle \hat{f}_r \rangle^{\mathbf{R}_{\rho g}}$ is the conditional expectation (3) for the present level of description.

The CG Hamiltonian $\mathcal{H}(\mathbf{R}, \rho, \mathbf{g})$ is shown in Appendix A, Eq. (A11) to be given rigorously as

$$\mathcal{H}(\mathbf{R}, \rho, \mathbf{g}) = -k_B T \ln \left\langle \frac{\exp \left\{ -\frac{\beta}{2} \mathbf{g}_\mu \hat{M}_{\mu\nu}^{-1} \mathbf{g}_\nu \right\}}{(2\pi/\beta)^{3M/2} \det \hat{M}^{3/2}} \right\rangle^{\mathbf{R}, \rho} + \mathcal{F}(\mathbf{R}, \rho) + \Phi^{\text{ext}}(\mathbf{R}) \quad (45)$$

In this expression the microscopic mass matrix is defined as

$$\hat{M}_{\mu\nu}(z) \equiv \sum_{i=0}^N m_i \delta_\mu(\mathbf{q}_i) \delta_\nu(\mathbf{q}_i) \quad (46)$$

This matrix depends on the microscopic configuration of the particles and we assume that for the typical configurations \mathbf{R}, ρ that condition the average in (45) are such that give microscopic configurations for which the inverse exists.

The fluid free energy is the sum of two contributions

$$\mathcal{F}(\mathbf{R}, \rho) = \mathcal{F}^{\text{sol}}(\rho^{\text{sol}}) + \mathcal{F}^{\text{int}}(\mathbf{R}, \rho^{\text{sol}}) \quad (47)$$

where the discrete solvent density ρ_μ^{sol} is defined in Eq. (21). The free energy of the solvent \mathcal{F}^{sol} and the free energy of interaction \mathcal{F}^{int} between nanoparticle and solvent are, respectively

$$\mathcal{F}^{\text{int}}(\mathbf{R}, \rho_{\text{sol}}) \equiv -k_B T \ln \left\langle \exp \left\{ -\beta \sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} - \mathbf{q}_i) \right\} \right\rangle^{\rho_{\text{sol}}}$$

(48)

where $P_{\text{sol}}^{\text{eq}}(\rho)$ is the equilibrium probability that a system without the nanoparticle has a particular realization ρ_μ for the mass density. The conditional expectation $\langle \dots \rangle^{\rho_{\text{sol}}}$ is an equilibrium average over solvent degrees of freedom conditional to give the realization ρ_μ for the discrete density. The fact that the free energy of the system in Eq. (47) depends on the mass density of the fluid ρ_μ through the combination ρ_μ^{sol} in (21), which is the mass density of the solvent in cell μ , is a non-trivial result.

B. Approximate results for the reversible drift

The exact but formal results (43), (45) need to be approximated in order to express them in terms of *explicit* functions of the relevant variables $\mathbf{R}, \rho_\mu, \mathbf{g}_\mu$. These re-

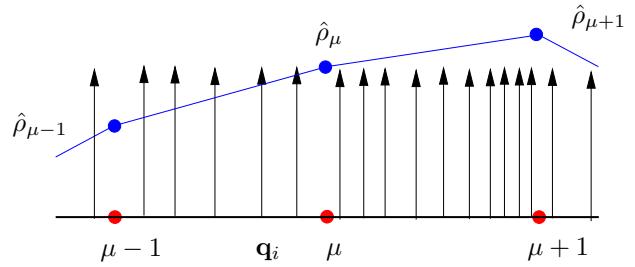


FIG. 3: The linear for spiky approximation: The microscopic density field $\hat{\rho}_r(z)$, which is a sum of Dirac delta functions, each located at the particle's position \mathbf{q}_i , is approximated with the linear interpolation $\psi_\mu(\mathbf{r})\hat{\rho}_\mu(z)$ (blue line) of the discrete values of the density field ρ_μ at the nodes.

sults involve conditional expectations of the microscopic density fields $\hat{\rho}_r(z)$, $\hat{g}_r(z)$. The basic approximation that we will consider when computing conditional averages of the microscopic mass and momentum density fields is that these fields may be approximated by linear interpolations of the CG densities, this is

$$\begin{aligned}\hat{\rho}_{\mathbf{r}}(z) &\simeq \psi_{\mu}(\mathbf{r})\hat{\rho}_{\mu}(z) \\ \hat{\mathbf{g}}_{\mathbf{r}}(z) &\simeq \psi_{\mu}(\mathbf{r})\hat{\mathbf{g}}_{\mu}(z)\end{aligned}\quad (49)$$

A graphical representation of this approximation in 1D is shown in Fig 3. Note that the approximation (49) is equivalent to replacing the Dirac delta function $\delta(\mathbf{r} - \mathbf{q}_i)$ in (19) with the regularized Dirac delta function $\Delta(\mathbf{r}, \mathbf{q}_i)$ introduced in (34).

We call this approximation *linear for spiky approximation* because $\hat{\rho}_r(z)$, as defined in Eq. (19), is a sum of Dirac delta functions while $\psi_\mu(\mathbf{r})\hat{\rho}_\mu(z)$ defined in (49) is a piece-wise linear function of space. The approximation assumes that for the “typically encountered” realization of ρ, \mathbf{g} , the above relation is well satisfied inside conditional expectations $\langle \dots \rangle^{\mathbf{R}\rho\mathbf{g}}$. It is obvious that such an approximation makes sense only if the conditioning values ρ_μ, \mathbf{g}_μ for the densities are such that they correspond to a sufficiently large number of particles in cell μ . Eqs. (49) need to be understood in the weak sense, this is, valid within expressions involving space integrals. Note that if we multiply both sides of the *approximate* equations (49) with $\delta_\nu(\mathbf{r})$ and integrate over space we get an *exact* identity $\hat{\rho}_\mu(z) = \hat{\rho}_\mu(z)$ for all microscopic states z ; this gives us confidence in the self-consistency of this approximation.

As we demonstrate in the Appendix, the linear for spiky approximation allows us to replace hatted functions with overlined functions, and to transform the double brackets $\llbracket \dots \rrbracket^{\mathbf{R}, \rho, \mathbf{g}}$ into simple space averages $\| \dots \|$. This transforms the exact results for the reversible drift into approximate but closed expressions, as we explain next.

1. Approximate mass matrix

The microscopic mass matrix $\hat{M}_{\mu\nu}(z)$ in (46) can be exactly expressed in terms of the microscopic field $\hat{\rho}_\mathbf{r}(z)$ introduced in (19),

$$\hat{M}_{\mu\nu}(z) = \|\delta_\mu \delta_\nu \hat{\rho}(z)\| \quad (50)$$

Note that this matrix satisfies the following exact results

$$\mathcal{V}_\mu \hat{M}_{\mu\nu}(z) = \hat{\rho}_\nu(z), \quad \mathcal{V}_\nu \hat{M}_{\mu\nu}(z) = \hat{\rho}_\mu(z) \quad (51)$$

where use has been made of the first equation (29).

Under the linear for spiky approximation (49), the mass matrix in (50) becomes

$$\hat{M}_{\mu\nu}(z) \simeq \|\delta_\mu \delta_\nu \psi_\sigma \| \hat{\rho}_\sigma(z) \quad (52)$$

and therefore, in this approximation the matrix $\hat{M}_{\mu\nu}(z)$ depends on the microstate z only through the *discrete* density field $\hat{\rho}_\sigma(z)$. The approximation (52) is consistent

in the sense that it fulfills the exact properties (51). Note that for a function of relevant variables $F(\hat{x}(z))$ the conditional expectations satisfies $\langle F(\hat{x}) \rangle^x = F(x)$. By using this property, the conditional expectation of the mass matrix (50) is

$$\langle \hat{M}_{\mu\nu} \rangle^{\mathbf{R}, \rho, \mathbf{g}} \simeq \|\delta_\mu \delta_\nu \psi_\sigma \| \rho_\sigma = \|\bar{\rho} \delta_\mu \delta_\nu \| \equiv \bar{M}_{\mu\nu}(\rho) \quad (53)$$

where the interpolated mass density field $\bar{\rho}(\mathbf{r})$ is defined in (42) and we have introduced the mass matrix $\bar{M}_{\mu\nu}(\rho)$ (with dimensions of mass over volume squared) for notational convenience.

2. Approximate reversible generator

In Appendix B, Eq. (B8), we show that under the linear for spiky approximations (49) the exact reversible drift originating from the reversible operator (43) becomes

$$\begin{pmatrix} \langle L\mathbf{R} \rangle^{\mathbf{R}, \rho, \mathbf{g}} \\ \langle L\rho_\mu \rangle^{\mathbf{R}, \rho, \mathbf{g}} \\ \langle L\mathbf{g}_\mu^\alpha \rangle^{\mathbf{R}, \rho, \mathbf{g}} \end{pmatrix} = \begin{pmatrix} 0 & 0 & \delta_\mu(\mathbf{R}) \\ 0 & 0 & \|\bar{\rho} \delta_\nu \nabla^\beta \delta_\mu\| \\ -\delta_\mu(\mathbf{R}) & -\|\bar{\rho} \delta_\mu \nabla^\alpha \delta_\nu\| & \|\bar{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu\| - \|\bar{\mathbf{g}}^\beta \delta_\mu \nabla^\alpha \delta_\nu\| \end{pmatrix} \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial \mathbf{R}} \\ \frac{\partial \mathcal{H}}{\partial \rho_\nu} \\ \frac{\partial \mathcal{H}}{\partial \mathbf{g}_\nu^\beta} \end{pmatrix} - k_B T \begin{pmatrix} 0 \\ 0 \\ -\nabla^\alpha \delta_\mu(\mathbf{R}) \end{pmatrix} \quad (54)$$

The interpolated density and velocity fields are defined as

$$\begin{aligned} \bar{\rho}(\mathbf{r}) &= \rho_\mu \psi_\mu(\mathbf{r}) \\ \bar{\mathbf{g}}(\mathbf{r}) &= \mathbf{g}_\mu \psi_\mu(\mathbf{r}) \end{aligned} \quad (55)$$

and the double bar notation introduced in (24) describes integration over all space. The stochastic drift proportional to $k_B T$ emerging from the divergence of the reversible matrix is very simple and, for the case of no suspended particles, indicates that the reversible dynamics follows a Hamiltonian dynamics, i.e., the phase space flow is incompressible.

3. Approximate CG Hamiltonian

In appendix C, see Eq. (C6), we show that under the linear for spiky approximation (52), the CG Hamiltonian (45) becomes

$$\mathcal{H}(\mathbf{R}, \rho, \mathbf{g}) = \frac{1}{2} \mathbf{g}_\mu \bar{M}_{\mu\nu}^{-1} \mathbf{g}_\nu + \mathcal{F}(\mathbf{R}, \rho) + \Phi^{\text{ext}}(\mathbf{R}) \quad (56)$$

The CG Hamiltonian is the free energy of the selected level of description, but we refer to it as a CG Hamiltonian because of the presence of a quadratic term in momenta that can be interpreted as a “kinetic energy” plus a “potential energy” given by the intrinsic fluid free energy $\mathcal{F}(\mathbf{R}, \rho)$. This free energy is given rigorously by (47).

In Appendix C, Eq. (C33) we introduce an explicit model for the free energy (47)

$$\mathcal{F}(\mathbf{R}, \rho) = \frac{c^2}{2\rho_{\text{eq}}} \delta\rho_\mu M_{\mu\nu}^\psi \delta\rho_\nu + \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \psi_\mu(\mathbf{R}) \rho_\mu \quad (57)$$

where $\delta\rho_\mu = \rho_\mu - \rho_{\text{eq}}$ is the density perturbation away from the average solvent density $\rho_{\text{eq}} = M_T / \mathcal{V}_T$, with \mathcal{V}_T being the total system volume. The motivation behind this model is that it gives Gaussian fluctuations for the solvent in the absence of any suspended nanoparticle, and describes in a CG manner the interaction between the nanoparticle and the solvent in such a way that gradients of density produce forces on the nanoparticle. The parameter c_0 with dimensions of speed governs the intensity of these forces. When the nanoparticle is simply a tagged solvent particle, $c_0 = c$.

The derivatives of the CG Hamiltonian (56) are computed in Appendix C, Eq. (C9)

$$\begin{aligned}\frac{\partial \mathcal{H}}{\partial \mathbf{R}} &= \frac{\partial \mathcal{F}}{\partial \mathbf{R}} + \frac{\partial \Phi^{\text{ext}}}{\partial \mathbf{R}} \\ \frac{\partial \mathcal{H}}{\partial \rho_\mu} &= -\frac{1}{2} \|\psi_\mu \bar{\mathbf{v}}\| + \frac{\partial \mathcal{F}}{\partial \rho_\mu} \\ \frac{\partial \mathcal{H}}{\partial \mathbf{g}_\mu} &= M_{\mu\mu'}^\psi \mathbf{v}_{\mu'}\end{aligned}\quad (58)$$

where the discrete velocity is defined as

$$\mathbf{v}_\mu \equiv M_{\mu\nu}^\delta \bar{M}_{\nu\nu'}^{-1} \mathbf{g}_{\nu'} \quad (59)$$

which is given in terms of the density dependent mass matrix and the momentum density field. The reason for introducing this somewhat involved definition for the hydrodynamic velocity is justified by the resulting form of the discrete hydrodynamic equations, resembling in form the structure of the continuum equations. Note that in an “incompressible” limit in which we assume that the density fluctuations are very small and then $\rho_\mu = \rho_{\text{eq}}$, the above expression simplifies to $\mathbf{v}_\mu = \rho_{\text{eq}}^{-1} \mathbf{g}_\mu$ because of

$$\bar{M}_{\mu\nu} = \|\bar{\rho} \delta_\mu \delta_\nu\| \simeq \rho_{\text{eq}} \|\delta_\mu \delta_\nu\| = \rho_{\text{eq}} M_{\mu\nu}^\delta. \quad (60)$$

Note that (59) may be written as

$$\begin{aligned}\mathbf{g}_\mu &\equiv \bar{M}_{\mu\nu} M_{\nu\nu'}^\psi \mathbf{v}_{\nu'} = \rho_\sigma \|\psi_\sigma \delta_\mu \delta_\nu\| M_{\nu\nu'}^\psi \mathbf{v}_{\nu'} \\ &= \|\delta_\mu \psi_\sigma \delta_\nu\| \rho_\sigma \mathbf{v}_\nu = \|\delta_\mu \bar{\rho} \bar{\mathbf{v}}\|\end{aligned}\quad (61)$$

This allows to write the interpolated momentum density field as

$$\bar{\mathbf{g}}(\mathbf{r}) = \psi_\mu(\mathbf{r}) \|\delta_\mu \bar{\rho} \bar{\mathbf{v}}\| \quad (62)$$

If we use (36) under an assumption of sufficiently smooth fields, which should apply in the limit when the grid cells are large and fluctuations are small, we obtain the *local* relationship

$$\bar{\mathbf{g}}(\mathbf{r}) \simeq \bar{\rho}(\mathbf{r}) \bar{\mathbf{v}}(\mathbf{r}) \quad (63)$$

which is the familiar continuum definition of velocity from the momentum and mass densities. In general, however, (63) does not hold identically and we prefer to define $\bar{\mathbf{v}}(\mathbf{r})$ as the interpolant based on the discrete velocities (59).

4. Approximate reversible drift

We may perform explicitly the matrix multiplication in Eq. (54) with (58). This leads to the following ap-

proximate form for the reversible drift

$$\begin{aligned}\langle L\mathbf{R} \rangle^{\mathbf{R}\rho\mathbf{g}} &= \bar{\mathbf{v}}(\mathbf{R}) \\ \langle L\rho_\mu \rangle^{\mathbf{R}\rho\mathbf{g}} &= \|\bar{\rho} \bar{\mathbf{v}} \cdot \nabla \delta_\mu\| \\ \langle L\mathbf{g}_\mu^\alpha \rangle^{\mathbf{R}\rho\mathbf{g}} &= \|\bar{\mathbf{g}} \bar{\mathbf{v}} \cdot \nabla \delta_\mu\| + k_B T \nabla \delta_\mu(\mathbf{R}) \\ &\quad - \delta_\mu(\mathbf{R}) \frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \|\bar{\rho} \delta_\mu \nabla \delta_\nu\| \frac{\partial \mathcal{F}}{\partial \rho_\nu} + \delta_\mu(\mathbf{R}) \mathbf{F}^{\text{ext}} \\ &\quad + \frac{1}{2} (\|\bar{\rho} \delta_\mu \nabla \delta_\nu\| \|\psi_\nu \bar{\mathbf{v}}^2\| - \|\bar{\rho} \delta_\mu \nabla \bar{\mathbf{v}}^2\|)\end{aligned}\quad (64)$$

By conforming to the structure (11), the reversible drift (64) preserves the equilibrium distribution function $e^{-\beta\mathcal{H}}$. The total mass (33) is conserved by the above equations, as a result of the identity (32). However, total momentum is not exactly conserved. Since in the molecular ensemble (14) momentum is conserved, it is important to conserve momentum strictly in the coarse-grained dynamics as well when $\mathbf{F}^{\text{ext}} = 0$, and we discuss this issue next.

The rate of change of the total momentum is given by

$$\begin{aligned}\frac{d\mathbf{P}_T}{dt} &= -\frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \|\bar{\rho} \nabla \delta_\nu\| \frac{\partial \mathcal{F}}{\partial \rho_\nu} \\ &\quad + \frac{1}{2} (\|\bar{\rho} \nabla \delta_\nu\| \|\psi_\nu \bar{\mathbf{v}}^2\| - \|\bar{\rho} \nabla \bar{\mathbf{v}}^2\|)\end{aligned}\quad (65)$$

which does not necessarily vanish. The violation of momentum conservation is weak, however. First, consider the velocity terms in (65). Under the assumption of smooth fields, Eq. (37) applies and shows that the difference of two terms in the parenthesis (last term in (65)) is small (second order in grid spacing). Therefore, we will neglect the last two term in the momentum equation in (64). Second, consider the terms involving the free energy in (65). We have shown in Eqs. (A14) and (B9) in the Appendices that the translational invariance of the microscopic Hamiltonian is reflected in the following approximate property of the free energy

$$\frac{\partial \mathcal{F}}{\partial \mathbf{R}} + \|\bar{\rho} \nabla \delta_\nu\| \frac{\partial \mathcal{F}}{\partial \rho_\nu} = 0 \quad (66)$$

relating the gradient of the free energy to the chemical potential $\frac{\partial \mathcal{F}}{\partial \rho_\mu}$. This identity implies the first two terms in (65) cancel. In a way reminiscent of Noether’s theorem, the microscopic translation invariance (66) implies total momentum conservation in Eq. (65).

Unfortunately, the model for the free energy (57) does not *strictly* respects the property (66). However, as we explain in Appendix C, we can restore the property (66) by making the plausible approximation that the density field is sufficiently smooth

$$\nabla \bar{\rho}(\mathbf{R}) \simeq \|\Delta \nabla \bar{\rho}\| \equiv \int d\mathbf{r} \Delta(\mathbf{R}, \mathbf{r}) \nabla \bar{\rho}(\mathbf{r}) \quad (67)$$

Recall that the reason why (67), which is an example

of (40), is not an exact identity is due to the fact that the regularized Dirac delta is not translation invariant, i.e. $\Delta(\mathbf{r}, \mathbf{r}') \neq \Delta(\mathbf{r} - \mathbf{r}')$; this is the origin of the (small) violation of momentum conservation. If we nevertheless assume that the approximation (67) is valid, then Eq. (66) is fulfilled as shown in Appendix C, Eq. (B10) and we restore exact momentum conservation.

In a similar spirit, the terms involving the free energy in the momentum equation are computed in Appendix C, in particular (C38), with the result

$$-\delta_\mu(\mathbf{R}) \frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \|\bar{\rho} \delta_\mu \nabla \delta_\nu\| \frac{\partial \mathcal{F}}{\partial \rho_\nu} = -\|\delta_\mu \nabla P\| \quad (68)$$

where we have introduced the “pressure” field

$$P(\mathbf{r}) = \frac{c^2}{2\rho_{\text{eq}}} (\bar{\rho}(\mathbf{r})^2 - \rho_{\text{eq}}^2) + m_0 \frac{(c_0^2 - c^2)}{\rho_{\text{eq}}} \Delta(\mathbf{R}, \mathbf{r}) \bar{\rho}(\mathbf{r}) \quad (69)$$

which consists of two parts, the first being the equation of state corresponding to the Gaussian model for the solvent free energy density, and the second one capturing the solvent-nanoparticle interaction. Note that this second contribution vanishes for a tagged fluid molecule, when $c_0 = c$.

Inserting the result (68) in (64) we get the final approximation of the reversible part of the momentum equation,

$$\begin{aligned} \langle L\mathbf{g}_\mu^\alpha \rangle^{\mathbf{R}\rho\mathbf{g}} &= \|\bar{\mathbf{g}} \cdot \nabla \delta_\mu\| + k_B T \nabla \delta_\mu(\mathbf{R}) \\ &\quad - \|\delta_\mu \nabla P\| + \delta_\mu(\mathbf{R}) \mathbf{F}^{\text{ext}} \end{aligned} \quad (70)$$

This form exactly conserves momentum, at the expense of breaking the structure (11). As a consequence, the equilibrium distribution that results from using the momentum conserving (70) instead of (64) will be slightly different from $\propto e^{-\beta\mathcal{H}}$. Note that even if we has exactly $e^{-\beta\mathcal{H}}$, the model of the free energy (57) leads to the a marginal equilibrium distribution of the particle position that is not given by the Gibbs-Boltzmann distribution $\exp\{-\beta\Phi^{\text{ext}}(\mathbf{R})\}$ but rather by (C43).

IV. THE IRREVERSIBLE PART OF THE DYNAMICS

The dissipative matrix (6) involves the projected currents $\delta L\hat{x} = L\hat{x}(z) - \langle L\hat{x} \rangle^{\hat{x}(z)}$, where $\hat{x}(z) = \{\hat{\mathbf{R}}, \hat{\rho}_\mu(z), \hat{\mathbf{g}}_\mu(z)\}$ and LX are the time derivatives of the relevant variables. They are obtained by applying the Liouville operator on the position of the nanoparticle, mass and momentum local densities. In order to compute the time derivatives of the CG hydrodynamic variables it is useful to first consider the time derivatives of the microscopic local fields $\hat{\rho}_\mathbf{r}(z), \hat{\mathbf{g}}_\mathbf{r}(z)$ defined in (19) which are

standard [45]. For pair-wise interactions they are

$$\begin{aligned} L\hat{\rho}_\mathbf{r}(z) &= -\nabla \cdot \hat{\mathbf{g}}_\mathbf{r}(z) \\ L\hat{\mathbf{g}}_\mathbf{r}(z) &= -\nabla \cdot \hat{\sigma}_\mathbf{r} + \mathbf{F}^{\text{ext}}(\mathbf{q}_0) \delta(\mathbf{q}_0 - \mathbf{r}) \end{aligned} \quad (71)$$

where the stress tensor has the standard form

$$\begin{aligned} \hat{\sigma}_\mathbf{r} &= \sum_{i=0}^N \mathbf{p}_i \mathbf{v}_i \delta(\mathbf{q}_i - \mathbf{r}) \\ &\quad + \frac{1}{2} \sum_{i,j=0}^N \mathbf{q}_{ij} \mathbf{F}_{ij} \int_0^1 d\epsilon \delta(\mathbf{r} - \mathbf{q}_i + \epsilon \mathbf{q}_{ij}) \end{aligned} \quad (72)$$

Note that the stress tensor includes the nanoparticle $i = 0$ in its definition.

The time derivatives of the relevant variables $\hat{\rho}_\mu(z), \hat{\mathbf{g}}_\mu(z)$ can be obtained with (20) from the time derivatives of $\hat{\rho}_\mathbf{r}(z), \hat{\mathbf{g}}_\mathbf{r}(z)$. They are given by

$$\begin{aligned} L\mathbf{R} &= \frac{\mathbf{p}_0}{m_0} \\ L\hat{\rho}_\mu(z) &= \sum_{i=0}^N \mathbf{p}_i \cdot \nabla \delta_\mu(\mathbf{q}_i) = \int d\mathbf{r} \nabla \delta_\mu(\mathbf{r}) \cdot \hat{\mathbf{g}}_\mathbf{r}(z) \\ L\hat{\mathbf{g}}_\mu(z) &= \int d\mathbf{r} \nabla \delta_\mu(\mathbf{r}) \cdot \hat{\sigma}_\mathbf{r}(z) + \mathbf{F}^{\text{ext}}(\mathbf{q}_0) \delta_\mu(\mathbf{q}_0) \end{aligned} \quad (73)$$

The corresponding reversible part $\langle L\hat{x} \rangle^{\hat{x}(z)}$ that is subtracted in the projected current has been computed in Eq. (64).

We will discuss shortly the projected current corresponding to the position of the colloid, which will be denoted by $\delta L\hat{\mathbf{R}} \equiv \delta\hat{\mathbf{V}}$. By using the linear for spiky approximation (49), we can approximate the time derivative of the density variable in (73) as follows

$$L\hat{\rho}_\mu(z) \simeq \int d\mathbf{r} \psi_\nu(\mathbf{r}) \nabla \delta_\mu(\mathbf{r}) \cdot \hat{\mathbf{g}}_\nu(z) \quad (74)$$

In this approximation, the time derivative of a relevant variable (the density) is itself given in terms of a relevant variable (the momentum). Therefore, the corresponding projected current vanishes, i.e. $\delta\rho_\mu(z) = 0$, resulting in a great simplification of the dissipative matrix. From Eq. (73), the projected current corresponding to the momentum may be expressed in the form

$$\delta L\hat{\mathbf{g}}_\mu(z) = \int d\mathbf{r} \nabla \delta_\mu(\mathbf{r}) \cdot \delta\hat{\sigma}_\mathbf{r} \quad (75)$$

where the fluctuations of the stress tensor are

$$\delta\hat{\sigma}_\mathbf{r} \equiv \hat{\sigma}_\mathbf{r}(z) - \langle \hat{\sigma}_\mathbf{r} \rangle^{\hat{\mathbf{R}}\hat{\rho}\hat{\mathbf{g}}} \quad (76)$$

The external force term in Eq. (73) disappears from the projected current (75) because it is just a function of $\mathbf{q}_0 = \mathbf{R}$ which is a relevant variable.

By using (75), we can write the dissipative matrix $\mathcal{D}(x)$

as a collection of Green-Kubo integrals

$$\boxed{\left(\begin{array}{ccc} \left\langle \delta \hat{\mathbf{V}}^\beta(0) \delta \hat{\mathbf{V}}^\alpha(t) \right\rangle^{\hat{\mathbf{R}} \hat{\rho} \hat{\mathbf{g}}} & 0 & \int d\mathbf{r}' \nabla^{\beta'} \delta_\nu(\mathbf{r}') \left\langle \delta \hat{\sigma}_{\mathbf{r}'}^{\beta \beta'}(0) \delta \hat{\mathbf{V}}^\alpha(t) \right\rangle^{\mathbf{R} \rho \mathbf{g}} \\ \frac{1}{k_B T} \int_0^\tau dt \left(\begin{array}{ccc} 0 & 0 & 0 \\ \int d\mathbf{r} \nabla^{\alpha'} \delta_\mu(\mathbf{r}') \left\langle \delta \hat{\mathbf{V}}^\beta(0) \delta \hat{\sigma}_{\mathbf{r}'}^{\alpha \alpha'}(t) \right\rangle^{\mathbf{R} \rho \mathbf{g}} & 0 & \int d\mathbf{r} \int d\mathbf{r}' \left\langle \delta \hat{\sigma}_{\mathbf{r}'}^{\beta \beta'}(0) \delta \hat{\sigma}_{\mathbf{r}}^{\alpha \alpha'}(t) \right\rangle^{\hat{\mathbf{R}} \hat{\rho} \hat{\mathbf{g}}} (\nabla^{\alpha'} \delta_\mu(\mathbf{r}) \nabla^{\beta'} \delta_\nu(\mathbf{r}')) \end{array} \right) \end{array} \right) \quad (77)}$$

In general, the dissipative matrix depends on the values of the coarse-grained variables $\mathbf{R}, \rho, \mathbf{g}$ that condition the expectation values in (77). Consider, for example, the colloid diffusion tensor defined as

$$\mathbf{D}(x) = \left\langle \delta \hat{\mathbf{V}}(0) \delta \hat{\mathbf{V}}(t) \right\rangle^{\hat{\mathbf{R}} \hat{\rho} \hat{\mathbf{g}}} = \int_0^\tau dt \frac{\rho^{\text{eq}}(z) \delta(\hat{x}(z) - x)}{P^{\text{eq}}(x)} \delta \hat{\mathbf{V}}(0) \delta \hat{\mathbf{V}}(t) \quad (78)$$

Indeed, even for a dilute nanocolloidal suspensions, had we tried to jump to the Smoluchowski level (using only the position of the nanocolloids as a slow variable) directly, the diffusion tensor would depend strongly on the configuration because of the hydrodynamic interactions (correlations) between the particles. At our level of description, however, we can assume that, to a good approximation, the dissipative matrix does not depend on the configuration and can be approximated by its *equilibrium average*, i.e., by replacing the conditional expectations in (77) with equilibrium averages. In this approxi-

mation,

$$\mathbf{D}(x) \simeq \mathbf{D}^{\text{eq}} \equiv \int dx' P^{\text{eq}}(x') \mathbf{D}(x') \quad (79)$$

By inserting (78) into (79) and integrating over the Dirac delta function gives

$$\mathbf{D}^{\alpha \beta}(x) \simeq \int_0^\tau dt \left\langle \delta \hat{\mathbf{V}}^\beta(0) \delta \hat{\mathbf{V}}^\alpha(t) \right\rangle_{\text{eq}} \quad (80)$$

where the average is now an ordinary equilibrium ensemble average rather than a constrained one.

Under the approximation in which the dissipative matrix is substituted by its equilibrium average, the non-diagonal elements of the dissipative matrix (77), which involve a third order tensor, will vanish because the equilibrium ensemble is isotropic and the only isotropic third order tensor is the null one. The dissipative matrix becomes

$$\boxed{\mathcal{D}(x) = \left(\begin{array}{ccc} \int_0^\tau dt \left\langle \delta \hat{\mathbf{V}}^\beta(0) \delta \hat{\mathbf{V}}^\alpha(t) \right\rangle_{\text{eq}} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \int d\mathbf{r} \int d\mathbf{r}' \eta_{\mathbf{r}\mathbf{r}'}^{\alpha \alpha' \beta \beta'} \nabla^{\alpha'} \delta_\mu(\mathbf{r}) \nabla^{\beta'} \delta_\nu(\mathbf{r}') \end{array} \right) \quad (81)}$$

where we have introduced a fourth order tensorial non-local viscosity kernel

$$\eta_{\mathbf{r}\mathbf{r}'}^{\alpha \alpha' \beta \beta'} \equiv \frac{1}{k_B T} \int_0^\tau dt \left\langle \delta \hat{\sigma}_{\mathbf{r}'}^{\beta \beta'}(0) \delta \hat{\sigma}_{\mathbf{r}}^{\alpha \alpha'}(t) \right\rangle^{\text{eq}} \quad (82)$$

A. Mass diffusion

The projected current corresponding to the position is given by

$$\delta L \hat{\mathbf{R}} = \hat{\mathbf{V}} - \hat{\mathbf{v}}^{\text{hydro}} \equiv \delta \hat{\mathbf{V}} \quad (83)$$

where we have denoted by $\hat{\mathbf{V}} = L\hat{\mathbf{R}} = \frac{\mathbf{p}_0}{m_0}$ the velocity of the nanoparticle. The term $\hat{\mathbf{v}}^{\text{hydro}}$ is the reversible part of the evolution of \mathbf{R} , given in the first equation in (64), evaluated at the microscopic value of the phase functions, this is

$$\hat{\mathbf{v}}^{\text{hydro}}(z) = \left\langle L\hat{\mathbf{R}} \right\rangle^{\hat{\mathbf{R}}\hat{\rho}\hat{\mathbf{g}}} = \psi_\mu(\hat{\mathbf{R}}) M_{\mu\nu}^\delta \bar{M}_{\nu\nu'}^{-1}(\hat{\rho}(z)) \hat{\mathbf{g}}_{\nu'}(z) \quad (84)$$

We expect that, being an equilibrium average, which is rotationally invariant, the tensor $\mathbf{D}(x)$ given in (80) is, in fact, diagonal and of the form

$$\mathbf{D}^{\alpha\beta} = D_0 \delta^{\alpha\beta} \quad (85)$$

Here the scalar *bare diffusion coefficient* is given by

$$D_0 = \frac{1}{d} \int_0^\tau dt \left\langle \delta\hat{\mathbf{V}}(0) \cdot \delta\hat{\mathbf{V}}(t) \right\rangle_{\text{eq}} \quad (86)$$

where d is the dimensionality, and $\delta\hat{\mathbf{V}}$ is defined in (83) with (84) as the fluctuation of the velocity of the nanoparticle relative to the surrounding flow velocity.

Note that the bare diffusion coefficient is different from the macroscopic or *renormalized diffusion coefficient*,

$$D = \frac{1}{d} \int_0^\tau dt \left\langle \hat{\mathbf{V}}(0) \cdot \hat{\mathbf{V}}(t) \right\rangle^{\text{eq}} \quad (87)$$

defined *without* subtracting the interpolated fluid velocity. We can split the renormalized diffusion coefficient into two parts [11], the bare part which comes from under-resolved details of the dynamics occurring at length and time scales shorter than the ones explicitly represented by the discrete hydrodynamic grid, and an enhancement ΔD that comes from the advection by the thermal velocity fluctuations and accounts for hydrodynamic transport explicitly resolved by the discrete grid,

$$\begin{aligned} D &= D_0 + \Delta D = D_0 \\ &+ \frac{1}{d} \int_0^\tau dt \left\langle \hat{\mathbf{v}}^{\text{hydro}}(0) \cdot \hat{\mathbf{v}}^{\text{hydro}}(t) \right. \\ &\left. + \hat{\mathbf{v}}^{\text{hydro}}(0) \cdot \delta\hat{\mathbf{V}}(t) + \delta\hat{\mathbf{V}}(0) \cdot \hat{\mathbf{v}}^{\text{hydro}}(t) \right\rangle^{\text{eq}} \end{aligned} \quad (88)$$

Observe that ΔD contains a lot of hydrodynamic information because of the time lag in the time correlation function; during the time t hydrodynamic information (sound waves, viscous dissipation, etc.) propagates around the particle and affects its diffusion coefficient.

As we elaborate in more detail in the Conclusions, the bare diffusion coefficient (86) depends on the size of the hydrodynamic cells, i.e., on the resolution at which hydrodynamics is represented. By contrast, the renormalized diffusion coefficient (87) is independent of the resolution of the grid. However, as mentioned in the introduction, D is not really computable in practice in MD, as opposed to D_0 , since the upper time limit τ should be

much larger in (87) than in (86).

B. Momentum Diffusion

The range of the viscous kernel given in (82) is that of the correlation length of the stress tensor. We will assume that this range is much smaller than the size of the cells, i.e. in the length scale in which $\eta_{\mathbf{r}\mathbf{r}'}$ is different from zero, the function $\nabla\delta_\mu(\mathbf{r})$ hardly changes. Note that the stress tensor (72) contains the contribution of the colloidal particle. Therefore, a condition for this locality assumption is that the colloidal particle itself is much smaller than the grid size. If this is the case, then we may adopt a local approximation

$$\eta_{\mathbf{r}\mathbf{r}'} \simeq \eta \delta(\mathbf{r} - \mathbf{r}') \quad (89)$$

and therefore the viscous contribution to the dissipative matrix (81) is

$$\begin{aligned} &\int d\mathbf{r} \int d\mathbf{r}' \eta_{\mathbf{r}\mathbf{r}'}^{\alpha\alpha'\beta\beta'} \nabla^{\alpha'} \delta_\mu(\mathbf{r}) \nabla^{\beta'} \delta_\nu(\mathbf{r}') \\ &\simeq \eta^{\alpha\alpha'\beta\beta'} \|\nabla^{\alpha'} \delta_\mu \nabla^{\beta'} \delta_\nu\| \end{aligned} \quad (90)$$

The explicit microscopic expression for η in (89) is obtained by integrating the viscosity kernel over \mathbf{r}, \mathbf{r}' to get

$$\int d\mathbf{r} \int d\mathbf{r}' \eta_{\mathbf{r}\mathbf{r}'}^{\alpha\alpha'\beta\beta'} \equiv \frac{1}{k_B T} \int_0^\tau dt \left\langle \delta\hat{\boldsymbol{\sigma}}^{\beta\beta'}(0) \delta\hat{\boldsymbol{\sigma}}^{\alpha\alpha'}(t) \right\rangle^{\text{eq}} \quad (91)$$

where the stress tensor of the whole system is, from (72)

$$\hat{\boldsymbol{\sigma}}^{\beta\beta'} = \int d\mathbf{r} \hat{\boldsymbol{\sigma}}_{\mathbf{r}}^{\beta\beta'} = \sum_{i=0}^N \mathbf{p}_i^\beta \mathbf{v}_i^{\beta'} + \frac{1}{2} \sum_{i,j=0}^N \mathbf{q}_{ij}^\beta \mathbf{F}_{ij}^{\beta'} \quad (92)$$

By using (89) into (91) gives

$$\eta^{\alpha\alpha'\beta\beta'} \equiv \frac{1}{k_B T \mathcal{V}_T} \int_0^\tau dt \left\langle \delta\hat{\boldsymbol{\sigma}}^{\beta\beta'}(0) \delta\hat{\boldsymbol{\sigma}}^{\alpha\alpha'}(t) \right\rangle^{\text{eq}} \quad (93)$$

where \mathcal{V}_T is the volume of the system.

The viscosity tensor, being an equilibrium correlation, will be isotropic. The general form of the isotropic fourth order tensor that accounts for the symmetries of the stress tensor appearing in the Green-Kubo expression is

$$\begin{aligned} \eta^{\alpha\alpha'\beta\beta'} &\equiv \eta \left(\delta^{\alpha\beta} \delta^{\alpha'\beta'} + \delta^{\alpha\beta'} \delta^{\beta\alpha'} - \frac{2}{d} \delta^{\alpha\alpha'} \delta^{\beta\beta'} \right) \\ &+ \zeta \delta^{\alpha\alpha'} \delta^{\beta\beta'} \end{aligned} \quad (94)$$

where η, ζ are shear and bulk viscosities, respectively. In practice, one would typically neglect the contribution of the nanoparticles to the viscous stress and assume that η, ζ are the pure solvent equilibrium viscosities.

Finally, the dissipative matrix (81) becomes

$$\mathcal{D}(x) \simeq \begin{pmatrix} \frac{D_0}{k_B T} \delta^{\alpha\beta} & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \boldsymbol{\eta}^{\alpha\alpha'\beta\beta'} \|\nabla^{\alpha'} \delta_\mu \nabla^{\beta'} \delta_\nu\| \end{pmatrix} \quad (95)$$

Note the dissipative matrix is independent of the state of the system due to its approximation with its equilibrium average. As a result, the stochastic drift term $k_B T \partial_x \cdot \mathcal{D}(x)$ in Eq. (9) should be taken as zero in this approximation.

C. Noise terms

In order to construct the Ito SDE (9) for the present level of description, we need to specify the noise terms $\frac{d\tilde{\mathbf{R}}}{dt}, \frac{d\tilde{\rho}_\mu}{dt}, \frac{d\tilde{\mathbf{g}}_\mu}{dt}$. The variance of the noise is given by the Fluctuation-Dissipation balance (10) where the matrix $\mathcal{D}(x)$ is given by (95). From the structure of this matrix we may infer that $\frac{d\tilde{\rho}_\mu}{dt} = 0$ and

$$\begin{aligned} \left\langle \frac{d\tilde{\mathbf{R}}}{dt}(t) \frac{d\tilde{\mathbf{R}}}{dt}(t') \right\rangle &= 2k_B T D_0 \delta(t - t') \\ \left\langle \frac{d\tilde{\mathbf{g}}_\mu^\alpha}{dt}(t) \frac{d\tilde{\mathbf{g}}_\nu^\beta}{dt}(t') \right\rangle &= 2k_B T \boldsymbol{\eta}^{\alpha\alpha'\beta\beta'} \|\nabla^{\alpha'} \delta_\mu \nabla^{\beta'} \delta_\nu\| \delta(t - t') \end{aligned} \quad (96)$$

We need to produce next explicit linear combinations of white noise that give rise to the above variances. While the velocity noise term is very simple

$$\frac{d\tilde{\mathbf{R}}}{dt}(t) = \sqrt{2k_B T D_0} \mathbf{W}(t) \quad (97)$$

where $\mathbf{W}(t)$ is a white noise, the explicit form of the random force $\frac{d\tilde{\mathbf{g}}_\mu}{dt}$ is not so obvious and will be considered next.

The noise term in the theory of CG is just a modelling of the projected current appearing in the Green-Kubo expression (6) as a white noise. For this reason, it is useful to look at the structure of the projected current in Eq. (75)

$$\delta L \mathbf{g}_\mu^\alpha = M_{\mu\mu'}^\delta \int d\mathbf{r} \nabla^\beta \psi_{\mu'}(\mathbf{r}) \delta \hat{\sigma}_\mathbf{r}^{\alpha\beta} \quad (98)$$

We will model $\delta \hat{\sigma}_\mathbf{r}^{\alpha\beta}$ as a linear combination of white

noises of the following form [57]

$$\begin{aligned} \delta \hat{\sigma}_\mathbf{r}^{\alpha\beta} \simeq \boldsymbol{\Sigma}_\mathbf{r}^{\alpha\beta} &= \sqrt{2k_B T \eta} \left[\mathbf{W}_\mathbf{r}^{\alpha\beta}(t) - \delta^{\alpha\beta} \frac{1}{d} \sum_\mu \mathbf{W}_\mathbf{r}^{\mu\mu}(t) \right] \\ &+ \sqrt{\frac{k_B T \zeta}{d}} \delta^{\alpha\beta} \sum_\mu \mathbf{W}_\mathbf{r}^{\mu\mu}(t) \end{aligned} \quad (99)$$

where the symmetric white-noise tensor $\mathbf{W}_\mathbf{r}^{\mu\nu}$ satisfies

$$\begin{aligned} \langle \mathbf{W}_\mathbf{r}^{\mu\nu}(t) \mathbf{W}_{\mathbf{r}'}^{\mu'\nu'}(t') \rangle &= [\delta^{\mu\mu'} \delta^{\nu\nu'} + \delta^{\nu\mu'} \delta^{\mu\nu'}] \\ &\times \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \end{aligned} \quad (100)$$

It is straightforward to show that

$$\langle \delta \sigma_\mathbf{r}^{\alpha\beta}(t) \delta \sigma_{\mathbf{r}'}^{\mu\nu}(t') \rangle = 2k_B T \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \boldsymbol{\eta}^{\alpha\beta\mu\nu} \quad (101)$$

and, therefore, the correlation of the random stress is a white noise in space and time, proportional to the viscosity tensor. Now we use the following expression for the piece-wise constant gradient of the finite element linear basis functions [55]

$$\nabla \psi_\nu(\mathbf{r}) = \sum_{e_\nu} \mathbf{b}_{e_\nu} \theta_{e_\nu}(\mathbf{r}) \quad (102)$$

where e_ν labels each of the sub-elements of the node ν , \mathbf{b}_{e_ν} is a constant vector within the sub-element e_ν that is pointing towards the node ν and $\theta_{e_\nu}(\mathbf{r})$ is the characteristic function of the sub-element e_ν .

The projected current, can be written, therefore, as

$$\delta L \mathbf{g}_\mu^\alpha = M_{\mu\nu}^\delta \int d\mathbf{r} \sum_{e_\nu} \mathbf{b}_{e_\nu}^\beta \theta_{e_\nu}(\mathbf{r}) \delta \sigma_\mathbf{r}^{\alpha\beta}(t) \quad (103)$$

By using the model (99) for the projected stress tensor and equating the random term $\frac{d\tilde{\mathbf{g}}_\mu}{dt}$ with the projected current $\delta L \mathbf{g}_\mu$ we have the following explicit model for the random forces

$$\frac{d\tilde{\mathbf{g}}_\mu^\alpha}{dt}(t) = M_{\mu\nu}^\delta \sum_{e_\nu} \mathbf{b}_{e_\nu}^\beta \tilde{\boldsymbol{\Sigma}}_{e_\nu}^{\alpha\beta}(t) \quad (104)$$

where the random stress tensor of the sub-element e_ν is given by

$$\begin{aligned} \tilde{\boldsymbol{\Sigma}}_{e_\nu}^{\alpha\beta}(t) &= \sqrt{2k_B T \eta} \left[\mathbf{W}_{e_\nu}^{\alpha\beta}(t) - \delta^{\alpha\beta} \frac{1}{d} \sum_\mu \mathbf{W}_{e_\nu}^{\mu\mu}(t) \right] \\ &+ \sqrt{\frac{k_B T \zeta}{d}} \delta^{\alpha\beta} \sum_\mu \mathbf{W}_{e_\nu}^{\mu\mu}(t) \end{aligned} \quad (105)$$

Here, we have introduced a symmetric matrix of white

noise processes associated to each sub-element e_ν

$$\mathcal{W}_e^{\mu\nu}(t) \equiv \int d\mathbf{r} \theta_e(\mathbf{r}) \mathcal{W}_{\mathbf{r}}^{\mu\nu}(t) \quad (106)$$

These symmetric white-noise processes are independent among elements due to (100)

$$\langle \mathcal{W}_e^{\mu\nu}(t) \mathcal{W}_{e'}^{\mu'\nu'}(t') \rangle = \delta_{ee'} [\delta^{\mu\mu'} \delta^{\nu\nu'} + \delta^{\nu\mu'} \delta^{\mu\nu'}] \delta(t - t') \quad (107)$$

The noise term (104) is a discrete divergence of a discrete random stress tensor. The discrete random stress tensor $\tilde{\Sigma}_{e_\nu}$ is an independent stochastic process associated to each sub-element. It is a matter of calculation to check that the postulated noise term $d\tilde{\mathbf{g}}_\mu$ in (104,105) with the white noise per element $\mathcal{W}_e^{\mu\nu}(t)$ satisfying (107), gives precisely the FD balance in (96).

Note that the noise (104) contains the matrix $M_{\mu\nu}^\delta$, which is the inverse of $M_{\mu\nu}^\psi$ defined in (26). The elements of $M_{\mu\nu}^\psi$ are proportional to the volume (area in 2D) of the overlapping region between two hydrodynamic cells which, in turn, scales as the typical volume of the hydrodynamic cells. Therefore, the stochastic force $\frac{d\tilde{\mathbf{g}}_\mu^\alpha}{dt}(t)$ scales with the inverse of the square root of the cell size. Larger cells are subject to smaller fluctuations, in accordance with the usual concepts in equilibrium statistical mechanics.

V. FINAL APPROXIMATE DYNAMIC EQUATIONS

We now have all the ingredients to construct the SDE (9) for the chosen coarse-grained level of description. By collecting the reversible part (64) with (70) and irreversible part of the dynamics given by $\mathcal{D} \cdot \partial_x \mathcal{H}$ (where the dissipative matrix is (95) and the derivatives of the CG Hamiltonian are in (58)), the final SODEs for the selected CG variables are

$$\begin{aligned} \frac{d\mathbf{R}}{dt} &= \bar{\mathbf{v}}(\mathbf{R}) - \frac{D_0}{k_B T} \frac{\partial \mathcal{F}}{\partial \mathbf{R}} + \frac{D_0}{k_B T} \mathbf{F}^{\text{ext}} + \frac{d\tilde{\mathbf{R}}}{dt} \\ \frac{d\rho_\mu}{dt} &= \|\bar{\rho} \bar{\mathbf{v}} \cdot \nabla \delta_\mu\| \\ \frac{d\mathbf{g}_\mu}{dt} &= \|\bar{\mathbf{g}} \bar{\mathbf{v}} \cdot \nabla \delta_\mu\| + k_B T \nabla \delta_\mu(\mathbf{R}) - \|\delta_\mu \nabla P\| + \delta_\mu(\mathbf{R}) \mathbf{F}^{\text{ext}} \\ &\quad + \eta \|\delta_\mu \nabla^2 \bar{\mathbf{v}}\| + \left(\frac{\eta}{3} + \zeta\right) \|\delta_\mu \nabla (\nabla \cdot \bar{\mathbf{v}})\| + \frac{d\tilde{\mathbf{g}}_\mu}{dt} \end{aligned} \quad (108)$$

These equations are the main result of this paper. Recall that the double bar denotes the spatial average defined in (24), and the overlined symbols denote interpolated fields out of the discrete values as in, for example, $\bar{\mathbf{v}}(\mathbf{r}) = \mathbf{v}_\nu \psi_\nu(\mathbf{r})$, etc. The velocity \mathbf{v}_ν is given in terms of ρ_μ, \mathbf{g}_μ in (59). The pressure equation of state is given in (69)

and the gradient of the free energy (57) is given by

$$\frac{\partial \mathcal{F}}{\partial \mathbf{R}} = \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \nabla \bar{\rho}(\mathbf{R}) \simeq m_0 \frac{(c_0^2 - c^2)}{\rho_{\text{eq}}} \|\Delta \nabla \bar{\rho}\| \quad (109)$$

see (67) for the definition of the notation $\|\Delta \nabla \bar{\rho}\|$. The SDEs (108) are closed and explicit in the relevant variables.

A. Physical meaning of the different terms in the dynamic equations

The first equation in (108) governs the evolution of the position of the nanoparticle. The first term $\bar{\mathbf{v}}(\mathbf{R})$ is purely reversible and says that the nanoparticle follows the interpolated velocity field of the fluid. This is a purely kinematic effect due to the fact that the momentum of the fluid contains the contribution due to the nanoparticle. It has nothing to do with any force that the fluid may perform on the particle which are described by the second contribution. This contribution is proportional to the bare mobility $D_0/k_B T$, given in terms of the *bare* diffusion coefficient D_0 introduced in (86) through a Green-Kubo relation. This term involves the (minus) gradient of the free energy $\mathcal{F}(\mathbf{R}, \rho)$, which plays the role of a *potential of mean force* for the nanoparticle given explicitly in (109). As seen in (C30) the force due to the fluid on the nanoparticle involves the gradients of the solvent density. The presence of the two parameters c_0 , that is due entirely to interactions of the nanoparticle with the solvent particles, and c , which is due to interactions of the solvent particles with themselves alone, indicates that $-\frac{\partial \mathcal{F}}{\partial \mathbf{R}}$ is not simply the force that the solvent exerts on the nanoparticle. Note that in the limit when the nanoparticle becomes just a tagged solvent particle, which is realized for $c_0 \rightarrow c$, $-\frac{\partial \mathcal{F}}{\partial \mathbf{R}}$ given in (109) vanishes. The third term in the position equation in (108) is due to the external force that obviously affects the motion of the nanoparticle. Finally, the nanoparticle is subject to an explicit noise term $\frac{d\tilde{\mathbf{R}}}{dt}$ whose variance is given by the fluctuation-dissipation balance relation (96). This term will produce Brownian motion of the nanoparticle, *in addition* to the advection by the fluctuating velocity field $\bar{\mathbf{v}}(\mathbf{R})$. In order to not “double count” the noise in the Brownian motion of the particle [11], the diffusion coefficient that governs the amplitude of the random noise term $\frac{d\tilde{\mathbf{R}}}{dt}$ is given in terms of the *bare* diffusion coefficient D_0 in (86), and not by the renormalized diffusion coefficient D defined in (87).

The second equation in (108) gives the evolution for the discrete mass density ρ_μ and has the form of a discrete continuity equation. This evolution is purely reversible due to the fact that, very approximately, the time derivative of the mass density is given in terms of the momentum density, which is a relevant variable. Therefore, the projected current vanishes and so do the Green-Kubo coefficients, i.e., there are no Brenner diffusion terms, as

argued in [58].

The third equation in (108) governs the discrete momentum density \mathbf{g}_μ . It has the structure of a discrete version of the fluctuating isothermal compressible Navier-Stokes equations with some modifications due to the interactions with the nanoparticle. The first term in the momentum equation is a convective non-linear term quadratic in the discrete momenta, which corresponds to the usual convective term in the Navier-Stokes equations. The second term originates from the stochastic drift $k_B T \partial_x \cdot \mathbf{L}$ term and can be interpreted as an *osmotic pressure* term due to the presence of the nanoparticle. The third term is reminiscent of the pressure gradient term in the usual Navier-Stokes equations. The pressure equation of state is given by the pressure due to the Gaussian model for the solvent, plus a pressure correction term (proportional to the difference of the squares of the speeds of sound) that describes the interaction between the solvent and the nanoparticle. Finally, the term proportional to \mathbf{F}^{ext} in (108) describes the effect that, because the discrete momentum variable contains the contribution due to the nanoparticle, any external force on the nanoparticle will translate into a force on the fluid itself. All the terms discussed so far in the momentum equation are purely reversible. The only irreversible terms in the momentum equation are proportional to the viscosities η, ζ and correspond to the usual viscous terms involving second space derivatives in the Navier-Stokes equations. Finally, the term $d\tilde{\mathbf{g}}_\mu$ is the random forces with explicit form given in (105) and whose amplitudes are dictated by the fluctuation-dissipation balance in (96).

Note that when $c_0 = c$ a number of terms in the equations above drop out and the equations simplify considerably. This happens, for example, when the distinguished particle is simply a tagged fluid molecule. This may also be a good approximation for neutrally buoyant particles that do not have a strong chemical interaction with the surrounding fluid, and the majority of prior work in the literature has in fact used the simplified model $c_0 = c$, with the notable exception of [37].

B. Scope and general properties of the dynamic equations

The validity of the SODEs (108) is limited to situations in which the values ρ_μ, \mathbf{g}_μ of the relevant variables are such that give a large number of solvent particles per hydrodynamic cell and, at the same time, give values that do not differ very much from one cell to its neighbors. In other words, the interpolated fields $\bar{\rho}(\mathbf{r}), \bar{\mathbf{g}}(\mathbf{r})$ need to be smooth on the hydrodynamic cell length scale. These assumptions imply that the validity of the equations is restricted to situations in which *thermal fluctuations are small*. Correspondingly, we have assumed that the solvent density fluctuations are Gaussian. This precludes the study of other interesting phenomenology like liquid-

vapor phase transitions, for example. However, it is a sufficiently simple and physically realistic model in many situations of interest. Concerning the nanoparticle, it is assumed that it is smaller than the hydrodynamic cell and it is, therefore, a *subgrid* nanoparticle.

The SODE (108) conserve exactly the total mass of the system defined in (33). In the absence of external forces acting on the nanoparticle, $\mathbf{F}^{\text{ext}} = 0$, the total momentum is also exactly conserved by the equations. This is just a reflection of the definition (17) of the discrete mass and momentum “fields” in terms of the basis functions that satisfy the partition of unity property (29). Momentum conservation is a direct consequence of translational invariance and we restored exact momentum conservation in our approximate equations by restoring translational invariance of our free-energy model.

Discrete fluctuation-dissipation balance (DFDB) is a crucial property that has been carefully maintained in prior work that relied on phenomenological equations, see for example [59] or Appendix B of [38]. A key component of DFDB is the energy conservation property that any work done by the external forces on the suspended nanoparticle must be converted exactly into kinetic energy of the fluid. In the terminology of Refs. [29, 38, 59], this means that the linear operator (matrix) used to *interpolate* the (discrete) fluid velocity to the particle, as represented by the term $\mathbf{v}_\mu \psi_\mu(\mathbf{R})$ in the first equation of (108), is the adjoint of the linear operator used to *spread* the force applied on the particle to the fluid, as represented by the term $\delta_\mu(\mathbf{R}) \mathbf{F}^{\text{ext}}(\mathbf{R})$ in the last equation in (108). This energy conservation follows directly from the skew-symmetry of the reversible operator (54).

If the reversible drift were exactly in the form $L\partial_x \mathcal{H} - k_B T \partial_x \cdot \mathbf{L}$, it would automatically maintain DFDB, this is, the equilibrium distribution function would be $\propto e^{-\beta H}$. However, the smoothness approximation taken in order to arrive at the model (108) imply that this is true up to small second order terms in the lattice spacing. Our selection of the model for the free energy is not exactly translational invariant, i.e. it does not satisfy (66) exactly. If it were, as shown in Appendix C, then we would obtain that the marginal distribution $P^{\text{eq}}(\mathbf{R})$ for the position of the particle would be given exactly by the barometric law (reduced Gibbs-Boltzmann distribution),

$$P^{\text{eq}}(\mathbf{R}) \sim \exp \{ -\beta \Phi^{\text{ext}}(\mathbf{R}) \} \quad (110)$$

However, the violation of translation invariance implies that the resulting probability distribution is given by (C43) instead, and the true barometric distribution is obtained only in the incompressible limit $c \rightarrow \infty$ or if $c_0 = c$ (e.g., a tagged particle).

C. The continuum equations

We have obtained the SODEs (108) from the Theory of Coarse-Graining. It can be shown that the same equations can be obtained from a Petrov-Galerkin discretization (see [47] for an illustration using the same basis functions as used here) of the following system of stochastic *partial* differential equations (SPDEs)

$$\begin{aligned} \frac{d}{dt}\mathbf{R} &= \int d\mathbf{r} \Delta(\mathbf{r}, \mathbf{R}) \mathbf{v}(\mathbf{r}) \\ &\quad - \frac{D_0}{k_B T} \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \int d\mathbf{r} \Delta(\mathbf{R}, \mathbf{r}) \nabla \rho(\mathbf{r}) \\ &\quad + \frac{D_0}{k_B T} \mathbf{F}^{\text{ext}} + \frac{d\tilde{\mathbf{R}}}{dt} \\ \partial_t \rho(\mathbf{r}, t) &= -\nabla \cdot \mathbf{g} \\ \partial_t \mathbf{g}(\mathbf{r}, t) &= -\nabla \cdot (\mathbf{g} \mathbf{v}) - k_B T \nabla \Delta(\mathbf{r}, \mathbf{R}) \\ &\quad - \nabla P(\mathbf{r}) + \mathbf{F}^{\text{ext}} \Delta(\mathbf{r}, \mathbf{R}) \\ &\quad + \eta \nabla^2 \mathbf{v} + \left(\frac{\eta}{3} + \zeta\right) \nabla (\nabla \cdot \mathbf{v}) + \nabla \cdot \Sigma_r^{\alpha\beta} \end{aligned} \quad (111)$$

where $\mathbf{v} = \mathbf{g}/\rho$, and the pressure is given by

$$P(\mathbf{r}) = \frac{c^2}{2\rho_{\text{eq}}} (\rho(\mathbf{r})^2 - \rho_{\text{eq}}^2) + \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \Delta(\mathbf{R}, \mathbf{r}) \rho(\mathbf{r}) \quad (112)$$

The random velocity $d\tilde{\mathbf{R}}/dt$ is given in (97), and the random stress tensor $\Sigma_r^{\alpha\beta}$ is given in (99). The equations (111) are very closely related to phenomenological equations used in prior work [34, 37, 38], with some differences that we further discuss in the Conclusions.

The Petrov-Galerkin method in its most pedestrian form has three steps: 1) Multiply the equations (111) for the hydrodynamic fields with the basis functions $\delta_\mu(\mathbf{r})$ and integrate with respect to space. 2) Define the discrete variables $\rho_\mu = \int d\mathbf{r} \delta_\mu(\mathbf{r}) \rho(\mathbf{r})$, etc. 3) Approximate the fields in the right hand side of the equations (111) with the linear interpolations $\bar{\rho}(\mathbf{r}) = \psi_\mu(\mathbf{r}) \rho_\mu$, etc. This procedure applied to (111) then leads to (108). As an example, let us consider the first term in the equation of motion for the particle, representing the advection by the fluid velocity. Replacing the velocity with its linear interpolant we get

$$\begin{aligned} \int \mathbf{v}(\mathbf{r}) \Delta(\mathbf{r}, \mathbf{R}) d\mathbf{r} &\rightarrow \int \mathbf{v}_\mu \psi_\mu(\mathbf{r}) \Delta(\mathbf{r}, \mathbf{R}) d\mathbf{r} \\ &= \mathbf{v}_\mu \int \psi_\mu(\mathbf{r}) \Delta(\mathbf{r}, \mathbf{R}) d\mathbf{r} \\ &= \mathbf{v}_\mu \psi_\mu(\mathbf{R}) = \bar{\mathbf{v}}(\mathbf{R}), \end{aligned} \quad (113)$$

where we used the property (35). The right hand side is exactly our discretization (derived here from the microscopic dynamics!) of the term on the left hand side. The rest of the terms are discretized in a similar way.

VI. DISCUSSION AND CONCLUSIONS

By performing a systematic coarse-graining procedure based on the Zwanzing projection operator, we have derived a system of stochastic *ordinary* differential equations (108) describing the dynamics of a nano-sized particle immersed in a simple liquid. A key to the procedure was the use of a dual set of linear basis functions familiar from finite element methods (FEM) as a way to coarse-grain the microscopic degrees of freedom. Another key ingredient was the use of a “linear for spiky” weak approximation which replaces microscopic “fields”, i.e., sums of delta functions centered at the fluid molecules, with a linear interpolant in the FEM basis set. These two steps enabled us to obtain *closed* approximations for all of the terms in the reversible or non-dissipative dynamics, in a manner which gives them a clear physical interpretation and preserves the correct structure of the equations. Notably, the reversible dynamics preserves a discrete Gibbs-Boltzmann distribution to high accuracy. For the irreversible or dissipative dynamics, we approximated the constrained Green-Kubo expressions for the dissipation coefficients with their equilibrium averages, and assumed a local form for the viscous dissipation suitable when the hydrodynamic cells contain a large number of fluid molecules.

The coarse-grained equations we derived here can be seen as a particular Petrov-Galerkin FEM discretization of a system of continuum stochastic *partial* differential equations (111) coupling the familiar isothermal fluctuating Navier-Stokes (FNS) equations with the Brownian motion of the immersed particle. These equations are similar in structure to phenomenological equations used in a number of prior works [11, 28, 29, 34, 37–42], and therefore provide a justification for those types of models via the Theory of Coarse Graining. This is not just an academic exercise, but one that also has some important practical utility. First, our derivation provides Green-Kubo expressions for transport coefficients, notably, for the *bare* diffusion coefficient which was phenomenologically added in [33] as a way to account for under-resolved microscopic details that cannot be captured with a hydrodynamic approach. Our derivation also introduces novel terms that come from the microscopic interaction between the suspended particle and the liquid molecules; these terms give additional modeling capability to account for more microscopic information in the coarse-grained description. Another, perhaps unexpected, benefit of the microscopic derivation was that it lead directly to a discrete form of the divergence of the stochastic stress which obeys the fluctuation-dissipation balance relation. In more empirical approaches, such a structure has to be either guessed, or constructed from suitable discrete stochastic fluxes and a pair of discrete divergence and gradient operators that are skew adjoints of one another [60].

The coarse-graining procedure carried out here can be viewed as a *systematic* derivation of the isothermal FNS

equations from molecular dynamics. Formal derivations of these equations have been done before many times, see for example early work including non-linearities in [57, 61], however, these derivations lead either to linearized equations or to *ill-defined* nonlinear SPDEs exhibiting an *ultraviolet catastrophe*. As we argued in more detail in [47], the proper way to interpret such *formal* nonlinear SPDEs is to first *discretize* them by applying a systematic discretization procedure, for example, using a Petrov-Galerkin weak formulation. The justification for this prescription is the fact that here we obtain *exactly* the same set of discretized SPDEs by systematic coarse graining. This gives a direct *link* between the “bottom-up” approach of going from microscopic to mesoscopic equations, and the “top-down” approach in which one starts from continuum PDEs and formally adds white-noise stochastic forcing and then applies a standard computational fluid dynamics (CFD) method to the resulting equations. Renormalization techniques should be applied to the discrete equations rather than the continuum ones in order to systematically increase the coarse-graining scale from the mesoscopic to the macroscopic in order to recover a continuum limit, where predictions of physical quantities like space-time correlations do not depend on the lattice spacing h as $h \rightarrow 0$.

The crucial link between the top-down and bottom-up approaches was already foreseen in [46], and then explicitly demonstrated on a significantly simpler microscopic model in the Ph.D. thesis [56]. At the same time, the new derivation given here significantly improves on the earlier derivation [46], which did not consider a suspended nanoparticle, in three key ways. Firstly, here we account for the presence of a suspended particle. Secondly, by using a dual set of basis functions, the resulting discretization is second-order rather than first-order accurate as the earlier derivation based on a single set of basis functions [56]. Thirdly, in the present work the discrete equations (108) have a very precise relation to the continuum equations (111), rather than simply being reminiscent of *some* “sensible” discretization. We have given an *explicit* prescription of how to connect the two worlds of MD and CFD: use the same dual set of basis functions when coarse-graining as you do when discretizing. We believe this prescription can be applied to a variety of other problems, however, as this work shows, the bottom-up approach requires a lot more work to complete than the top-down approach.

A. Relation to phenomenological models

The continuum equations (111) we proposed here bear a strong similarity, but also some crucial differences, with existing models. In order to explain the relation to prior work more clearly, let us review a variety of existing models starting from more “refined” to more “coarse.” A more formal mathematical presentation of these levels of description is given by Atzberger [59], here we give a phys-

ical summary. In many works an incompressible approximations is made in order to eliminate fast sound waves from the model [38, 39]. If one is interested only in the long-time diffusive dynamics the fluid inertia can also be eliminated by taking an overdamped limit [11, 29, 42, 59]. Here we focus on the coupling between the nanocolloidal particle and the fluctuating fluid and not on the specifics of the fluid equations.

In a number of “point particle” *frictional* coupling approaches, as reviewed in detail in [41], the colloid’s velocity is also included as a physical variable and a phenomenological “friction” force proportional to the velocity of the colloid relative to the local fluid velocity is added to an inertial particle equation. As we discussed in more detail in Section II B, such a level of description is not suitable under our assumption that the colloid is smaller than the typical size of the hydrodynamic cells. Instead, we include the momentum of colloid in the *total* hydrodynamic momentum field. We note that, although not usually presented in this way, the same is actually true to a large extent for the model used in [41] because what is called the mass of the colloid is actually the *excess* mass of the colloid over the expelled fluid [34, 38]. This is because the inertia of the expelled fluid is already included in the FNS equations, which are assumed to apply everywhere including the volume occupied by the particle. Therefore, part of the momentum of the particle is in fact included in the “fluid momentum”. For this reason, we find it difficult to imagine how one can justify the frictional point particle coupling model from a microscopic derivation.

In [34, 38], an *instantaneous* inertial coupling is proposed in which the particle is forced to follow the local fluid velocity; the main difference is that [34] considers a compressible fluid, while [38] focuses on the incompressible limit. As shown in [62], the instantaneous coupling [34, 38] can be derived as a limit of the frictional coupling when the friction coefficient becomes very large. In the language of the TCG, the (fast) momentum of the particle is no longer included as a relevant variable, instead, just as in our description, a total momentum field is defined [38, 59]. This total momentum field follows an equation which has a similar structure to the momentum equation in (111), see for example Eq. (16) in [38] in the incompressible limit. It is important to note that, even in the limit of an incompressible liquid, the density ρ appearing in (111) is *not* constant, rather, it includes the contribution from the colloid. Therefore, for a dense particle (e.g., gold nanocolloid) the discrete density will be larger at the nodes in the vicinity of the particle. This “excess inertia” is explicitly included in the model in Refs. [34, 38] (see for example the left-hand side of (13) in [38]) by “spreading” the excess inertia to the fluid grid. In the equations derived here the excess inertia is hidden in the definition of the coarse-grained density to include the contribution from the colloid, and the fact that the equation of state is only applied to the solvent part of the density ρ^{sol} .

The terms in the particle equation related to the bare diffusion coefficient D_0 do not appear in either [34] or [59, 62]; these terms are suggested in Appendix B.1 of [38] but not included in numerical simulations. A bare diffusion coefficient is also introduced in the theoretical work [11] but it is argued there that this term should somehow be small. Interestingly, a renormalization of the diffusion coefficient similar in spirit to D_0 is present in the frictional coupling formulation [41] and can be expressed in the Einstein form $D_0 = k_B T / \gamma$, where γ is the phenomenological friction coefficient, see Eq. (290) in [41]. In the limit of infinite friction, which is how [59, 62] derives the instantaneous coupling equations, $D_0 \rightarrow 0$. However, this is “throwing the baby out with the bathwater” and is not consistent with our microscopic derivation. The fact that $D_0 > 0$ is easy to appreciate: the sum $D = D_0 + \Delta D$ is a physical parameter that can be measured and is independent of the grid spacing (i.e., the coarse-graining length scale) while $\Delta D < D$ depends *strongly* on the grid spacing, as we explain in more detail shortly. In our derivation, D_0 emerges naturally as does a Green-Kubo expression for it, giving it a precise microscopic interpretation. The fact our instantaneous coupling equations with bare diffusion cannot be consistently derived from the frictional coupling formulation [41] points to the lack of a microscopic foundation of that formulation, and justifies once again the advantage of systematic bottom-up approaches over phenomenological ones.

The stochastic thermal drift term $-k_B T \nabla \Delta(\mathbf{r}, \mathbf{R})$ in the momentum equation is (wrongly) missing in [34]; the term is also (rightfully) missing in the frictional coupling [41] formulation. This term ought to be there for instantaneous coupling, as explained in Appendix B of [38] based on fluctuation-dissipation balance arguments, and derived by taking the limit of infinite friction in the frictional coupling in [62]. This osmotic pressure contribution from the particle, spread to the fluid via the regularized delta function, can be seen as coming from the eliminated fluctuations of the particle velocity around the local fluid velocity [59, 62]. In the inertial coupling formulation, as explained in Appendix B of [38] and also in [37], this osmotic pressure is split into two pieces just like the particle momentum is split into two pieces, one piece attached to the fluid momentum and another excess piece. When the two pieces are added together one correctly recovers exactly the osmotic pressure term given in (111) [37].

The gradient of the solvent pressure appears in all phenomenological models, and seems very natural but it should be recognized that this is only an approximation. Notably, the approximation consists in the assumption that this pressure is given by the equation of state of the fluid in the *absence* of the colloidal particle. This approximation is exact for a labeled or tagged particle of the fluid, i.e., in case of self-diffusion. One can argue that the same should *approximately* hold for colloidal particles that have a similar structure to the fluid, notably, that

have the same density and compressibility as the fluid. Balboa *et al.* [37] have proposed adding an additional excess pressure term to account for a different compressibility of the colloid relative to the surrounding fluid, see (116). These terms are postulated on a phenomenological basis.

In this work we derived equations containing similar terms, however, as already explained, our model for the free energy differs from that used in [37] and our final equations (111) are different from their, which can be written in our notation as

$$\frac{d}{dt} \mathbf{R} = \int \Delta(\mathbf{R} - \mathbf{r}) \mathbf{v}(\mathbf{r}) \, d\mathbf{r}, \quad (114)$$

$$\partial_t \rho = -\nabla \cdot \mathbf{g}, \quad (115)$$

$$\partial_t \mathbf{g} = -\nabla \cdot (\mathbf{g} \mathbf{v}) - (k_B T) \nabla \Delta(\mathbf{R} - \mathbf{r}) - \nabla P + \mathbf{F}^{\text{ext}} \Delta(\mathbf{R} - \mathbf{r}) + \nabla \cdot \boldsymbol{\sigma}. \quad (116)$$

where

$$P = c^2(\rho(\mathbf{r}) - \rho_{\text{eq}}) + \mathcal{V}(c_0^2 - c^2) \Delta(\mathbf{R} - \mathbf{r}) \int \Delta(\mathbf{R} - \mathbf{r}') (\rho(\mathbf{r}') - \rho_{\text{eq}}) \, d\mathbf{r}' \quad (117)$$

where the regularized delta function $\Delta(\mathbf{R}, \mathbf{r}) = \Delta(\mathbf{R} - \mathbf{r})$ is given by a Gaussian-like isotropic kernel $\Delta(r)$ of width comparable to the hydrodynamic radius of the nanoparticle and that integrates to unity. Here the fluid velocity is defined via $\mathbf{v} = \mathbf{g}/\rho$, and $\boldsymbol{\sigma}$ denotes the viscous stress (deterministic and fluctuating components) with a form identical to ours. The volume associated to the particle can be expressed in our notation as $\mathcal{V} \equiv m_0/\rho_{\text{eq}}$ but is interpreted differently in [37] to be a geometric rather than an inertial quantity. Note that we have set here the excess mass of the particle [37] over the fluid $m_e = 0$ because in our notation ρ includes the total mass of the particle (see additional discussion in Section VI).

The similarities between our formulation and the formulation of Balboa *et al.* are evident, but there are also some notable differences. The equations (116) do not include bare diffusion (i.e., $D_0 = 0$) and therefore a number of terms are missing from the particle equation. In the model of Ref. [37] the parameter c_0 is used to represent the speed of sound (i.e., the isothermal compressibility) inside the colloidal particle, while in our model c_0 models the mean force that the colloid experiences in a density gradient, see (C30). Balboa *et al.* justify the “particle compressibility” pressure contribution proportional to $c_0^2 - c^2$ starting from a *quadratic* contribution to the free energy density of the form

$$\mathcal{F}_{\text{comp}} = \frac{\mathcal{V}(c_0^2 - c^2)}{2\rho_{\text{eq}}} \left(\int \Delta(\mathbf{R} - \mathbf{r}') (\rho(\mathbf{r}') - \rho_0) \, d\mathbf{r}' \right)^2$$

whereas the “continuum” analog of our *linear* model for the interaction free energy found in the last term in (57)

is

$$\mathcal{F}_{\text{int}} = \mathcal{V}(c_0^2 - c^2) \left(\int \Delta(\mathbf{R} - \mathbf{r}') (\rho(\mathbf{r}') - \rho_0) d\mathbf{r}' \right)$$

It is important to emphasize, however, that our discussion of similarities to prior work above only concerns the formal continuum formulation (111) and focuses on the structure of the equations and the physics of the various terms. Our fully *discrete* formulation (108) is completely new and is different in many crucial ways from existing discretizations. The first difference is that the discretization of the FNS equations is based on a second-order conservative FEM method, rather than the more commonly used finite-difference [39] or finite-volume approach [60]. A second difference is that in all prior models we are aware of, the regularized delta function is used to represent the particle itself, and its width is chosen to be on the order of the hydrodynamic radius of the particle. As such, the regularized delta function is attached to the *particle*, i.e., it is taken to be a smeared delta function kernel such as a Gaussian kernel or the tensor-product kernel of Peskin [63] centered at the particle position. By contrast, in the formulation (111) the regularized delta function represents the coarsening of the solvent dynamics and its width is assumed to be larger than the subgrid colloidal particle. As such, our discrete delta function kernel is attached to the *grid* and is not centered around the particle; this is most obvious in (108) where it is clearly seen that in the equation for the (fixed in space) grid node μ the regularization enters via the basis function δ_μ associated to that node. Note that in the immersed-boundary formulation of Peskin used in a number of prior works [29, 34, 37–39, 41] the *width* of the discrete delta function is tied to the grid spacing just as it is for our regularized delta function, however, in those prior works the regularized kernel is still centered around the particle. This was proposed by Peskin as a very effective way to maximize translational invariance of the particle-grid interactions [63]; we expect our formulation will not perform as well in terms of translational invariance because it was not explicitly constructed with that goal in mind.

B. Renormalization of the diffusion coefficient

Let us consider, for a moment, a single freely-diffusing isolated spherical nanoparticle suspended in a quiescent fluid. At large time scales, the particle will perform a standard Brownian motion with a renormalized diffusion coefficient D given in (87) by the familiar Green-Kubo integral of the particle's velocity autocorrelation function. Since this quantity only involves the nanoparticle position, it cannot depend on how we chose to perform the coarse graining of the fluid. In particular, it must be a number independent of the typical grid spacing h . For sufficiently large Schmidt numbers [33] we expect it to be well-predicted by the Stokes-Einstein formula (in

three dimensions)

$$D \approx D_{\text{SE}} = \frac{k_B T}{\alpha \eta R},$$

where R is the radius of the spherical particle and α is a coefficient that depends on the boundary conditions applicable at the surface of the sphere, equal to 6π for a stick surface and 4π for a slip surface, or something in-between for more realistic models [64, 65].

In the fluctuating hydrodynamic formalism presented here, the renormalized diffusion coefficient D is split into a bare part D_0 and a renormalization ΔD defined by (88). Let us try to get a more quantitative understanding of the diffusion enhancement ΔD for our specific discretization (approximation) of the equations. First, we can replace the instantaneous interpolated fluid velocity $\hat{\mathbf{v}}^{\text{hydro}}$ by its approximation $\bar{\mathbf{v}}(\mathbf{R}) = \mathbf{v}_\mu \psi_\mu(\mathbf{R})$. Second, we can ignore the cross-correlation terms since $\hat{\mathbf{V}}$ evolves on a much faster time scale than the hydrodynamic fields and can be assumed to be a white-noise process uncorrelated with $\bar{\mathbf{v}}(\mathbf{R})$. This gives the approximation to the diffusion enhancement produced by our discrete equations,

$$\begin{aligned} \Delta D(\mathbf{R}) &= \frac{1}{d} \int_0^\tau dt \langle \bar{\mathbf{v}}(\mathbf{R}(0)) \cdot \bar{\mathbf{v}}(\mathbf{R}(t)) \rangle^{\text{eq}} \\ &= \frac{1}{d} \int_0^\tau dt \langle \psi_\mu(\mathbf{R}(0)) (\mathbf{v}_\mu(0) \cdot \mathbf{v}_{\mu'}(t)) \psi_{\mu'}(\mathbf{R}(t)) \rangle^{\text{eq}}. \end{aligned} \quad (118)$$

In the overdamped limit of large Schmidt numbers (see [33] for corrections at moderate Schmidt numbers), the particle moves much slower than the hydrodynamic correlations decay, and one can express the diffusion enhancement in terms of the *equilibrium* correlation of the fluid velocity (conditional on the particle being fixed at a particular location),

$$\Delta D(\mathbf{R}) = \frac{1}{d} \int_0^\infty dt \psi_\mu(\mathbf{R}) \langle \mathbf{v}_\mu(0) \cdot \mathbf{v}_{\mu'}(t) \rangle_{\mathbf{R}}^{\text{eq}} \psi_{\mu'}(\mathbf{R}), \quad (119)$$

which can in principle be computed exactly by linearizing the fluid equations around a quiescent state. Note that ΔD depends on \mathbf{R} explicitly; for confined systems this dependence is physical but for translationally invariant system such dependence is a discretization artifact that is hopefully small. Note that the immersed-boundary discrete delta function used in Refs. [29, 34, 37–39] is specifically designed to obtain such translational invariance on regular grids to a high accuracy [63].

We can obtain a physical estimate for the diffusion due to advection by the thermal velocity fluctuations by assuming that the discrete velocities are consistent with a Petrov-Galerkin procedure applied to continuum equations. This allows us to approximate the discrete velocity \mathbf{v}_μ in terms of a continuum fluctuating field $\mathbf{v}(\mathbf{r}, t)$ as $\mathbf{v}_\mu(t) = \int d\mathbf{r} \delta_\mu(\mathbf{r}) \mathbf{v}(\mathbf{r}, t)$. If we substitute this in (119)

we obtain the estimate

$$\begin{aligned}
\Delta D(\mathbf{R}) &= \int d\mathbf{r} d\mathbf{r}' \psi_\mu(\mathbf{R}) \delta_\mu(\mathbf{r}) \\
&\times \left(\frac{1}{d} \int_0^\infty dt \langle \mathbf{v}(\mathbf{r}, 0) \cdot \mathbf{v}(\mathbf{r}', t) \rangle^{\text{eq}} \right) \delta_{\mu'}(\mathbf{r}') \psi_{\mu'}(\mathbf{R}) \\
&= \int d\mathbf{r} d\mathbf{r}' \Delta(\mathbf{r}, \mathbf{R}) \\
&\times \left(\frac{1}{d} \int_0^\infty dt \langle \mathbf{v}(\mathbf{r}, 0) \cdot \mathbf{v}(\mathbf{r}', t) \rangle^{\text{eq}} \right) \Delta(\mathbf{r}', \mathbf{R}).
\end{aligned} \tag{120}$$

If one assumes that the evolution of $\mathbf{v}(\mathbf{r}, t)$ can be described by a fluctuating Stokes equation (i.e., linearized incompressible flow), the time integral can easily be expressed in terms of the inverse Stokes operator (i.e., the Green's function for Stokes flow) [33]. In this case the relation (120) can directly be matched with Eq. (10) in [33] (see also Eq. (288) in [41]), where the regularized delta function is denoted with $\Delta(\mathbf{r}, \mathbf{R}) \rightarrow \delta_a(\mathbf{r} - \mathbf{R})$. In our notation Eq. (10) in [33] becomes,

$$\begin{aligned}
\Delta D(\mathbf{R}) &= \frac{k_B T}{\eta} \int d\mathbf{r} d\mathbf{r}' \Delta(\mathbf{r}, \mathbf{R}) \\
&\times \left(\frac{1}{d} \text{Trace } \mathbf{G}(\mathbf{r}, \mathbf{r}') \right) \Delta(\mathbf{r}', \mathbf{R}),
\end{aligned} \tag{121}$$

where \mathbf{G} is the Green's function for Stokes flow (Oseen tensor for an unbounded domain at rest at infinity). This is nothing else but an Einstein formula relating the diffusion coefficient with the mobility of the particle, i.e., with the linear response of the particle to a weak applied force.

A simple calculation based on the expression for \mathbf{G} in Fourier space, or, equivalently, based on replacing the continuum Green's function with its discrete equivalent, estimates that in three dimensions [33]

$$\Delta D = \frac{k_B T}{\alpha' \eta h},$$

where h is the width of the regularized Delta function (i.e., the grid spacing), and α' is a coefficient that depends on the geometric details of the grid. This suggests that

$$D_0 = \frac{k_B T}{\eta} \left(\frac{1}{\alpha' h} - \frac{1}{\alpha R} \right),$$

which must be non-negative, i.e., it must be that $\alpha R < \alpha' h$, which is consistent with the assumption that the nanoparticle is smaller than a typical grid cell. Observe that at large Schmidt numbers ΔD can be expressed purely in terms of geometric quantities and the equilibrium (discrete) fluid correlation functions, and should therefore depend mildly if at all on the details of the interaction between the particle and the fluid. This suggests that it is the *bare* diffusion coefficient that must

capture essentially *all* of the microscopic details such as slip versus no-slip on the particle surface or layering of the fluid around the particle.

In the microscopic derivation presented here, the bare diffusion coefficient D_0 is to be computed using (86) from the Green-Kubo integral of the autocorrelation function of the particle *peculiar* velocity, i.e., the velocity relative to the local (interpolated) fluid velocity. Only a combination of molecular dynamics and fluctuating FEM calculations can tell us whether the effective diffusion coefficient $D = D_0 + \Delta D$ indeed be a constant (approximately) independent of the grid resolution. In prior work based on phenomenological fluctuating hydrodynamics theories [11], D_0 was treated as an adjustable parameter that is chosen so as to give a *desired* (input) effective D , since ΔD follows from the discretization of the fluid equations and cannot be adjusted independently. This is similar to how one can treat the fluid-particle interaction strength parameter c_0 as fitting parameters used to match the coarse-grained and particle dynamics as best as possible, instead of computing it from its (approximate!) microscopic definition (C23).

C. Future Directions

The work described here is purely theoretical and proposes a model with the correct structure but leaves a number of terms to be approximated and modeled. As such, the usefulness and accuracy of our equations cannot be judged until a number of numerical studies are performed.

Firstly, a temporal discretization needs to be developed to go with the spatial discretization (108); the required tools are readily available [66, 67]. Secondly, it is important to study the numerical aspects of the Petrov-Galerkin FEM discretization developed here using existing numerical analysis tools [60, 68] and compare to existing discretizations. Lastly, one needs to include immersed particles in the numerics as well and study a number of standard test problems to evaluate the performance of (108) as a standalone method for simulating dilute colloidal suspensions. Particular emphasis should be placed to the violations of discrete fluctuation dissipation balance and of translational invariance, both of which are in a formal sense second order in the grid spacing, but may be significant in practice at scales comparable to the grid spacing.

It is an important task for future work to perform molecular dynamics (MD) simulations and compare the results to the coarse-grained description proposed here. We expect that if the grid cells are too small we will see unphysical artifacts, and if the grid cells are too large, the MD simulations will become unfeasible. By confirming whether the correct effective (renormalized) diffusion coefficient is obtained over a reasonable range of grid spacings, we can access how good the approximations made in our coarse graining theory are, and ultimately how useful

the proposed equations are in practice. One should begin these studies with a single nanocolloidal particle in solvent in a periodic box of varying sizes, perhaps starting in two dimensions, where there are very strong (in fact, asymptotically dominant rather than decaying) finite size effects [11].

A key question that we did not fully address here is how to compute the various coefficients that appear in (108). We already discussed the subtlety of this issue for the bare diffusion coefficient. Even more freedom exists for the free energy of interaction between the solute and the solvent, which needs to be modeled with some number of adjustable parameters. These parameters are to be tuned by matching the coarse-grained and microscopic descriptions. How to do this matching in practice remains an important open question. We proposed a specific model with a single adjustable parameter here but it remains to be seen whether this model is appropriate on a case-by-case basis, and if not, to make adjustments to the equations by following the approach developed in this work.

It is important to emphasize here that (108) can be used to study colloidal suspensions of more than one colloidal particle, however, the description will only be accurate when the colloids are further than about one grid cell apart. This is because our modeling of the bare diffusion coefficient is based on equilibrium Green-Kubo expressions for a single particle. This will fail to give an accurate approximation when two particles come closer to each other than a grid spacing; at such short distances the hydrodynamic correlations among the diffusing particles will *not* be captured accurately. This is no different from prior work [11, 28, 29, 34, 37–41] where the hy-

drodynamic interactions are only resolved up to at most the Stokeslet or Rotne-Prager level. Furthermore, when the nanocolloids come close to each other we expect that their direct interactions with the solvent molecules or with each other will be affected and other terms in (108) will need to be modified as well. Ultimately, as the density is increased there will be many nanoparticles per hydrodynamic cell and in this case a coarse-grained theory of fluid mixtures should emerge. Such a theory could perhaps provide a bridge between macroscopic fluid mixture equations [24] and dynamic density functional theories with hydrodynamic effects [30–32].

Finally, the present theory is isothermal as the energy density of the fluid is assumed to be a fast decaying variable as compared with mass and momentum variables. Of course, this precludes the study of thermal processes that arise in nanocolloidal suspensions in the presence of thermal gradients. The formulation of non-isothermal models is the subject of ongoing work.

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APPENDIX A: DERIVATION OF EXACT RESULTS

In this appendix we obtain a number of exact results for the equilibrium probability distributions, the free energies, and the reversible drift term.

1. Equilibrium distributions

The equilibrium probability $P(x)$ in Eq. (4) in the present level of description takes the form

$$P^{\text{eq}}(\mathbf{R}, \rho, \mathbf{g}) = \int dz \frac{1}{Z} \exp\{-\beta \hat{H}(z)\} \delta(\mathbf{R} - \mathbf{q}_0) \prod_{\mu}^M \delta(\rho_{\mu} - \hat{\rho}_{\mu}(z)) \delta(\mathbf{g}_{\mu} - \hat{\mathbf{g}}_{\mu}(z)) \quad (\text{A1})$$

and the conditional expectation $\langle \dots \rangle^x$ in Eq. (3) takes the form

$$\langle \dots \rangle^{\mathbf{R}\rho\mathbf{g}} = \frac{1}{P^{\text{eq}}(\mathbf{R}, \rho, \mathbf{g})} \int dz \frac{1}{Z} \exp\{-\beta \hat{H}(z)\} \delta(\mathbf{R} - \mathbf{q}_0) \prod_{\mu}^M \delta(\rho_{\mu} - \hat{\rho}_{\mu}(z)) \delta(\mathbf{g}_{\mu} - \hat{\mathbf{g}}_{\mu}(z)) \dots \quad (\text{A2})$$

It is convenient to introduce the marginal equilibrium probability $P^{\text{eq}}(\mathbf{R}, \rho)$,

$$P^{\text{eq}}(\mathbf{R}, \rho) = \int dz \frac{1}{Z} \exp\{-\beta \hat{H}(z)\} \delta(\mathbf{R} - \mathbf{q}_0) \prod_{\mu}^M \delta(\rho_{\mu} - \hat{\rho}_{\mu}(z)) \quad (\text{A3})$$

and the corresponding conditional expectation $\langle \dots \rangle^{\mathbf{R}, \rho}$ conditional on \mathbf{R}, ρ , and not on \mathbf{g} . Finally, we will also consider the equilibrium probability distribution of the density field, in the absence of nanoparticle, which is defined as

$$P_{\text{sol}}^{\text{eq}}(\rho) \equiv \int \prod_{i=1}^N d\mathbf{q}_i d\mathbf{p}_i \frac{1}{Z^{\text{sol}}} \exp \left\{ -\beta \left(\sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \hat{U}^{\text{sol}}(q) \right) \right\} \prod_{\mu}^M \delta(\rho_{\mu} - \hat{\rho}_{\mu}^{\text{sol}}(z)) \quad (\text{A4})$$

where Z^{sol} is the normalization and the solvent mass density $\hat{\rho}_{\mu}^{\text{sol}}(z)$ is introduced in Eq. (18). The corresponding equilibrium expectation over solvent degrees of freedom conditional to the solvent density is denoted by $\langle \dots \rangle_{\text{sol}}^{\rho}$.

The three probabilities (A1), (A3), (A4) are related to each other. By integrating the momentum variables in (A1), occurring in the kinetic energy of the Hamiltonian and in the Dirac delta functions, with (E2) in the Appendix E we have

$$P^{\text{eq}}(\mathbf{R}, \rho, g) = \frac{1}{Z'} \int \prod_{i=0}^N d\mathbf{q}_i \exp\{-\beta \hat{U}(q)\} \delta(\mathbf{R} - \mathbf{q}_0) \prod_{\mu}^M \delta(\rho_{\mu} - \hat{\rho}_{\mu}(z)) \frac{\exp\left\{-\frac{\beta}{2} \mathbf{g}_{\mu} \hat{M}_{\mu\nu}^{-1}(z) \mathbf{g}_{\nu}\right\}}{(2\pi/\beta)^{3M/2} \det \hat{M}(z)^{3/2}} \quad (\text{A5})$$

where the mass matrix is defined in (46).

In a similar way, by integrating the atomic momenta in (A3), gives the following form for the marginal equilibrium probability

$$P^{\text{eq}}(\mathbf{R}, \rho) = \int \prod_{i=0}^N d\mathbf{q}_i \frac{1}{Q} \exp\left\{-\beta \hat{U}(q)\right\} \delta(\mathbf{R} - \mathbf{q}_0) \prod_{\mu}^M \delta(\rho_{\mu} - \hat{\rho}_{\mu}(z)) \quad (\text{A6})$$

where all momentum variables have been integrated out and Q is the normalization. We may write (A5) in the following form

$$P^{\text{eq}}(\mathbf{R}, \rho, g) = P^{\text{eq}}(\mathbf{R}, \rho) \left\langle \frac{\exp\left\{-\frac{\beta}{2} \mathbf{g}_{\mu} \hat{M}_{\mu\nu}^{-1} \mathbf{g}_{\nu}\right\}}{(2\pi/\beta)^{3M/2} \det \hat{M}^{3/2}} \right\rangle^{\mathbf{R}, \rho} \quad (\text{A7})$$

that gives the relation between $P^{\text{eq}}(\mathbf{R}, \rho, g)$ and $P^{\text{eq}}(\mathbf{R}, \rho)$.

At the same time, the marginal $P^{\text{eq}}(\mathbf{R}, \rho)$ in Eq. (A3) can be expressed in terms of the probability distribution of the solvent density $P_{\text{sol}}^{\text{eq}}(\rho)$ in the absence of nanoparticle. First, integrate momenta in (A4) to get

$$P_{\text{sol}}^{\text{eq}}(\rho) \equiv \int \prod_{i=1}^N d\mathbf{q}_i \frac{1}{Q^{\text{sol}}} \exp\left\{-\beta \hat{U}^{\text{sol}}(z)\right\} \prod_{\mu}^M \delta(\rho_{\mu} - \hat{\rho}_{\mu}^{\text{sol}}(z)) \quad (\text{A8})$$

where Q^{sol} is the normalization. Then, Eq. (A6) becomes

$$\begin{aligned} P^{\text{eq}}(\mathbf{R}, \rho) &= \int \prod_{i=1}^N d\mathbf{q}_i \frac{1}{Q} \exp \left\{ -\beta \left(\hat{U}^{\text{sol}}(z) + \sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} - \mathbf{q}_i) + \Phi^{\text{ext}}(\mathbf{R}) \right) \right\} \prod_{\mu}^M \delta(\rho_{\mu} - m_0 \delta_{\mu}(\mathbf{R}) - \hat{\rho}_{\mu}^{\text{sol}}(z)) \\ &= \frac{1}{Q'} P_{\text{sol}}^{\text{eq}}(\rho - m_0 \delta(\mathbf{R})) \left\langle \exp \left\{ -\beta \int d\mathbf{r} \Phi^{\text{int}}(\mathbf{R} - \mathbf{r}) \hat{n}_{\mathbf{r}}^{\text{sol}} \right\} \right\rangle_{\text{sol}}^{\rho - m_0 \delta(\mathbf{R})} \exp\{-\beta \Phi^{\text{ext}}(\mathbf{R})\} \end{aligned} \quad (\text{A9})$$

where in the first equality we have integrated the Dirac delta function $\delta(\mathbf{R} - \mathbf{q}_0)$ and in the second equality we have used the definition (A8).

2. Free energies

The relationships (A7) and (A9) between the probabilities reflects into an exact expression for the free energy of the system. Let us introduce the free energy of the solvent $\mathcal{F}^{\text{sol}}(\rho)$, the free energy of the fluid $\mathcal{F}(\mathbf{R}, \rho)$, and the CG Hamiltonian $\mathcal{H}(\mathbf{R}, \rho, g)$ (which is also a free energy) through the following expressions

$$\begin{aligned} P_{\text{sol}}^{\text{eq}}(\rho) &\propto \exp\{-\beta\mathcal{F}^{\text{sol}}(\rho)\} \\ P^{\text{eq}}(\mathbf{R}, \rho) &\propto \exp\{-\beta\mathcal{F}(\mathbf{R}, \rho) - \beta\Phi^{\text{ext}}(\mathbf{R})\} \\ P^{\text{eq}}(\mathbf{R}, \rho, g) &\propto \exp\{-\beta\mathcal{H}(\mathbf{R}, \rho, g)\} \end{aligned} \quad (\text{A10})$$

We now look at the relationships between these free energies (up to irrelevant constants). Because of (A7) and (A9), the CG Hamiltonian has the form

$$\mathcal{H}(\mathbf{R}, \rho, \mathbf{g}) = -k_B T \ln \left\langle \frac{\exp\left\{-\frac{\beta}{2}\mathbf{g}_\mu \hat{M}_{\mu\nu}^{-1} \mathbf{g}_\nu\right\}}{(2\pi/\beta)^{3M/2} \det \hat{M}^{3/2}} \right\rangle^{\mathbf{R}, \rho} + \mathcal{F}(\mathbf{R}, \rho) + \Phi^{\text{ext}}(\mathbf{R}) \quad (\text{A11})$$

and the fluid free energy is

$$\mathcal{F}(\mathbf{R}, \rho) = \mathcal{F}^{\text{sol}}(\rho - m_0 \delta(\mathbf{R})) + \mathcal{F}^{\text{int}}(\mathbf{R}, \rho - m_0 \delta(\mathbf{R})) \quad (\text{A12})$$

where the free energy of interaction between nanoparticle and solvent is

$$\mathcal{F}^{\text{int}}(\mathbf{R}, \rho) \equiv -k_B T \ln \left\langle \exp\left\{-\beta \int d\mathbf{r} \Phi^{\text{int}}(\mathbf{R} - \mathbf{r}) \hat{n}_{\mathbf{r}}^{\text{sol}}\right\} \right\rangle_{\text{sol}}^{\rho} \quad (\text{A13})$$

The exact result (A12) that decomposes the free energy of the system into a solvent and an interaction part will be very useful for modelling. The fact that the free energy depends on ρ_μ only through the combination $\rho_\mu^{\text{sol}} = \rho_\mu - m_0 \delta_\mu(\mathbf{R})$, which is the mass density of the solvent, is a non-trivial result.

3. The role of translation invariance on the free energy

In this appendix we demonstrate the following exact identity involving derivatives of the free energy

$$\frac{\partial \mathcal{F}}{\partial \mathbf{R}}(\mathbf{R}, \rho) = k_B T \frac{\partial}{\partial \rho_\nu} [\hat{\rho} \nabla \delta_\nu]^{\mathbf{R}, \rho} - [\hat{\rho} \nabla \delta_\nu]^{\mathbf{R}, \rho} \frac{\partial \mathcal{F}}{\partial \rho_\nu} \quad (\text{A14})$$

This identity is a direct consequence of translation invariance of the microscopic Hamiltonian. It is an important result because it gives an exact relationship between the derivatives of the free energy with respect to \mathbf{R} and ρ_μ . This mathematical identity gives a strong condition on the modelling of the free energy.

The proof is as follows. In the integrals over positions in (A3) perform the change of variables $\mathbf{q}_i = \mathbf{q}'_i - \mathbf{a}$ which is a pure translation. The solvent potential is translation invariant and, therefore,

$$\begin{aligned} P^{\text{eq}}(\mathbf{R}, \rho) &= \int \prod_{i=1}^N d\mathbf{q}'_i \frac{1}{Q} \exp \left\{ -\beta \left(\hat{U}^{\text{sol}}(q) + \sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} + \mathbf{a} - \mathbf{q}'_i) + \Phi^{\text{ext}}(\mathbf{R}) \right) \right\} \\ &\times \prod_{\mu}^M \delta \left(\rho_\mu - m_0 \delta_\mu(\mathbf{R}) - \sum_{i=1}^N m \delta_\mu(\mathbf{q}'_i - \mathbf{a}) \right) \end{aligned} \quad (\text{A15})$$

Note that the right hand side does not depend really on \mathbf{a} . Take the derivative with respect to \mathbf{a} and multiply by

$k_B T$ to obtain

$$\begin{aligned}
0 = & \int \prod_{i=0}^N d\mathbf{q}'_i \frac{1}{Q} \exp \left\{ -\beta \left(\hat{U}^{\text{sol}}(q) + \sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} + \mathbf{a} - \mathbf{q}'_i) + \Phi^{\text{ext}}(\mathbf{R}) \right) \right\} \int d\mathbf{r} \mathbf{F}^{\text{int}}(\mathbf{R} + \mathbf{a} - \mathbf{r}) \hat{n}_{\mathbf{r}}^{\text{sol}}(z) \\
& \times \prod_{\mu}^M \delta \left(\rho_{\mu} - m_0 \delta_{\mu}(\mathbf{R}) - \sum_{i=1}^N m \delta_{\mu}(\mathbf{q}'_i - \mathbf{a}) \right) \\
& + k_B T \int \prod_{i=0}^N d\mathbf{q}'_i \frac{1}{Q} \exp \left\{ -\beta \left(\hat{U}^{\text{sol}}(q) + \sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} + \mathbf{a} - \mathbf{q}'_i) + \Phi^{\text{ext}}(\mathbf{R}) \right) \right\} \\
& \times \sum_{\nu} \frac{\partial}{\partial \rho_{\nu}} \int d\mathbf{r} \nabla \delta_{\nu}(\mathbf{r} - \mathbf{a}) \hat{\rho}_{\mathbf{r}}^{\text{sol}}(z) \prod_{\mu}^M \delta \left(\rho_{\mu} - m_0 \delta_{\mu}(\mathbf{R}) - \sum_{i=1}^N m \delta_{\mu}(\mathbf{q}'_i - \mathbf{a}) \right) \tag{A16}
\end{aligned}$$

Here, $\mathbf{F}^{\text{int}}(\mathbf{R} - \mathbf{r})$ is the force that a solvent particle located at \mathbf{r} exerts on the nanoparticle located at \mathbf{R} . Evaluate this expression at $\mathbf{a} = 0$ and divide by $P^{\text{eq}}(\mathbf{R}, \rho)$ to obtain

$$0 = \int d\mathbf{r} \mathbf{F}^{\text{int}}(\mathbf{R} - \mathbf{r}) \langle \hat{n}_{\mathbf{r}}^{\text{sol}} \rangle^{\mathbf{R} \rho} + k_B T \int d\mathbf{r} \sum_{\nu} \nabla \delta_{\nu}(\mathbf{r}) \frac{1}{P^{\text{eq}}(\mathbf{R}, \rho)} \frac{\partial}{\partial \rho_{\nu}} P^{\text{eq}}(\mathbf{R}, \rho) \langle \hat{\rho}_{\mathbf{r}}^{\text{sol}} \rangle^{\mathbf{R} \rho} \tag{A17}$$

Therefore, translation invariance implies the following exact result

$$\int d\mathbf{r} \mathbf{F}^{\text{int}}(\mathbf{R} - \mathbf{r}) \langle \hat{n}_{\mathbf{r}}^{\text{sol}} \rangle^{\mathbf{R} \rho} = -k_B T \frac{\partial}{\partial \rho_{\nu}} [\hat{\rho}^{\text{sol}} \nabla \delta_{\nu}]^{\mathbf{R} \rho} + [\hat{\rho}^{\text{sol}} \nabla \delta_{\nu}]^{\mathbf{R} \rho} \frac{\partial}{\partial \rho_{\nu}} \mathcal{F}(\mathbf{R}, \rho) \tag{A18}$$

where we have used the notation (44). This result is important because it relates the actual force on the nanoparticle due to the solvent with the derivatives of the free energy.

Now, the gradient of the free energy $\mathcal{F}(\mathbf{R}, \rho)$ introduced in Eq. (A10) satisfies

$$\begin{aligned}
\frac{\partial}{\partial \mathbf{R}} \mathcal{F}(\mathbf{R}, \rho) + \frac{\partial}{\partial \mathbf{R}} \Phi^{\text{ext}}(\mathbf{R}) = & -\frac{1}{P^{\text{eq}}(\mathbf{R}, \rho)} \int \prod_{i=1}^N d\mathbf{q}_i \frac{1}{Q} \exp \left\{ -\beta \left(\hat{U}^{\text{sol}}(q) + \sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} - \mathbf{q}_i) - \beta \Phi^{\text{ext}}(\mathbf{R}) \right) \right\} \\
& \times \int d\mathbf{r} \mathbf{F}^{\text{int}}(\mathbf{R} - \mathbf{r}) \hat{n}_{\mathbf{r}}^{\text{sol}}(z) \prod_{\mu}^M \delta \left(\rho_{\mu} - m_0 \delta_{\mu}(\mathbf{R}) - \sum_{i=1}^N m_i \delta_{\mu}(\mathbf{q}_i) \right) \\
& - k_B T \frac{1}{P^{\text{eq}}(\mathbf{R}, \rho)} \int \prod_{i=1}^N d\mathbf{q}_i \frac{1}{Q} \exp \left\{ -\beta \left(\hat{U}^{\text{sol}}(q) + \sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} - \mathbf{q}_i) - \beta \Phi^{\text{ext}}(\mathbf{R}) \right) \right\} \\
& \times \sum_{\nu} \frac{\partial}{\partial \rho_{\nu}} (-m_0 \nabla \delta_{\nu}(\mathbf{R})) \prod_{\mu}^M \delta \left(\rho_{\mu} - m_0 \delta_{\mu}(\mathbf{R}) - \sum_{i=1}^N m_i \delta_{\mu}(\mathbf{q}_i) \right) \tag{A19}
\end{aligned}$$

Hence we have the exact result

$$\begin{aligned}
\mathbf{F}(\mathbf{R}) &= \int d\mathbf{r} \mathbf{F}^{\text{int}}(\mathbf{R} - \mathbf{r}) \langle \hat{n}_{\mathbf{r}}^{\text{sol}} \rangle^{\mathbf{R} \rho} \\
&= -\frac{\partial \mathcal{F}}{\partial \mathbf{R}}(\mathbf{R}, \rho) - m_0 \nabla \delta_{\nu}(\mathbf{R}) \frac{\partial \mathcal{F}}{\partial \rho_{\nu}}(\mathbf{R}, \rho) \tag{A20}
\end{aligned}$$

This result shows that the force on the nanoparticle due to the solvent is not simply the gradient of the free energy $-\frac{\partial \mathcal{F}}{\partial \mathbf{R}}(\mathbf{R}, \rho)$, but also depends on the chemical potential of the fluid near the particle. This is because the density includes the mass of the colloid in our formulation. The two exact result (A18) and (A20) combine to give the exact relation (A14).

4. The exact form of the reversible drift

We now consider the form of the drift given by (11). The Poisson brackets entering the elements of the re-

versible matrix are computed as follows

$$\begin{aligned}
\{\hat{\mathbf{R}}, \hat{\mathbf{R}}\} &= 0 \\
\{\hat{\mathbf{R}}, \hat{\rho}_\nu\} &= 0 \\
\{\hat{\mathbf{R}}, \hat{\mathbf{g}}_\nu\} &= \delta_\mu(\mathbf{r}_0) \\
\{\hat{\rho}_\mu, \hat{\mathbf{R}}\} &= 0 \\
\{\hat{\mathbf{g}}_\mu, \hat{\mathbf{R}}\} &= -\delta_\mu(\mathbf{r}_0) \\
\{\hat{\rho}_\mu, \hat{\rho}_\nu\} &= \sum_i \frac{\partial \hat{\rho}_\mu}{\partial \mathbf{r}_i} \frac{\partial \hat{\rho}_\nu}{\partial \mathbf{p}_i} - \frac{\partial \hat{\rho}_\mu}{\partial \mathbf{p}_i} \frac{\partial \hat{\rho}_\nu}{\partial \mathbf{r}_i} = 0
\end{aligned} \tag{A21}$$

$$\begin{aligned}
\{\hat{\rho}_\mu, \hat{\mathbf{g}}_\nu\} &= \sum_i m_i \delta_\nu(\mathbf{r}_i) \nabla \delta_\mu(\mathbf{r}_i) \\
&= \int d\mathbf{r} \hat{\rho}_\mathbf{r}(z) \delta_\nu(\mathbf{r}) \nabla \delta_\mu(\mathbf{r}) \\
\{\hat{\mathbf{g}}_\mu, \hat{\rho}_\nu\} &= - \sum_i m_i \delta_\mu(\mathbf{r}_i) \nabla \delta_\nu(\mathbf{r}_i) \\
&= \int d\mathbf{r} \hat{\rho}_\mathbf{r}(z) \delta_\mu(\mathbf{r}) \nabla \delta_\nu(\mathbf{r}) \\
\{\hat{\mathbf{g}}_\mu^\alpha, \hat{\mathbf{g}}_\nu^\beta\} &= \sum_i \left(\mathbf{p}_i^\alpha \delta_\nu(\mathbf{r}_i) \nabla^\beta \delta_\mu(\mathbf{r}_i) - \mathbf{p}_i^\beta \delta_\mu(\mathbf{r}_i) \nabla^\alpha \delta_\nu(\mathbf{r}_i) \right) \\
&= \int d\mathbf{r} \left[\hat{\mathbf{g}}_\mathbf{r}^\alpha \delta_\nu(\mathbf{r}) \nabla^\beta \delta_\mu(\mathbf{r}) - \hat{\mathbf{g}}_\mathbf{r}^\beta \delta_\mu(\mathbf{r}) \nabla^\alpha \delta_\nu(\mathbf{r}) \right]
\end{aligned} \tag{A22}$$

The conditional averages are

$$\begin{aligned}
\left\langle \left\{ \hat{\mathbf{R}}, \hat{\mathbf{g}}_\nu \right\} \right\rangle^{\mathbf{R}^{\rho^B} \mathbf{g}^B} &= \delta_\mu(\mathbf{R}) \\
\left\langle \left\{ \hat{\rho}_\mu, \hat{\mathbf{g}}_\nu \right\} \right\rangle^{\mathbf{R}^{\rho^B} \mathbf{g}^B} &= [\hat{\rho} \delta_\nu \nabla \delta_\mu]^{\mathbf{R}^{\rho \mathbf{g}}} \\
\left\langle \left\{ \hat{\mathbf{g}}_\mu^\alpha, \hat{\mathbf{g}}_\nu^\beta \right\} \right\rangle^{\mathbf{R}^{\rho^B} \mathbf{g}^B} &= [\hat{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu]^{\mathbf{R}^{\rho \mathbf{g}}} - [\hat{\mathbf{g}}^\beta \delta_\mu \nabla^\alpha \delta_\nu]^{\mathbf{R}^{\rho \mathbf{g}}}
\end{aligned} \tag{A23}$$

where the double bracket notation is introduced in (44). Therefore, the reversible part of the dynamics takes the form

$$\begin{aligned}
\begin{pmatrix} \left\langle L \hat{\mathbf{R}} \right\rangle^{\mathbf{R}^{\rho \mathbf{g}}} \\ \left\langle L \hat{\rho}_\mu \right\rangle^{\mathbf{R}^{\rho \mathbf{g}}} \\ \left\langle L \hat{\mathbf{g}}_\mu^\alpha \right\rangle^{\mathbf{R}^{\rho \mathbf{g}}} \end{pmatrix} &= \begin{pmatrix} 0 & 0 & \delta_\mu(\mathbf{R}) \\ 0 & 0 & [\hat{\rho} \delta_\nu \nabla^\beta \delta_\mu]^{\mathbf{R}^{\rho \mathbf{g}}} \\ -\delta_\mu(\mathbf{R}) & -[\hat{\rho} \delta_\mu \nabla^\alpha \delta_\nu]^{\mathbf{R}^{\rho \mathbf{g}}} & [\hat{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu]^{\mathbf{R}^{\rho \mathbf{g}}} - [\hat{\mathbf{g}}^\beta \delta_\mu \nabla^\alpha \delta_\nu]^{\mathbf{R}^{\rho \mathbf{g}}} \end{pmatrix} \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial \mathbf{R}} \\ \frac{\partial \mathcal{H}}{\partial \rho_\nu} \\ \frac{\partial \mathcal{H}}{\partial \mathbf{g}_\nu^\beta} \end{pmatrix} \\
&- k_B T \begin{pmatrix} 0 \\ \frac{\partial}{\partial \mathbf{g}_\nu^\alpha} [\hat{\rho} \delta_\nu \nabla^\alpha \delta_\mu]^{\mathbf{R}^{\rho \mathbf{g}}} \\ -\nabla^\alpha \delta_\mu(\mathbf{R}) - \frac{\partial}{\partial \rho_\nu} [\hat{\rho} \delta_\mu \nabla^\alpha \delta_\nu]^{\mathbf{R}^{\rho \mathbf{g}}} + \frac{\partial}{\partial \mathbf{g}_\nu^\beta} ([\hat{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu]^{\mathbf{R}^{\rho \mathbf{g}}} - [\hat{\mathbf{g}}^\beta \delta_\mu \nabla^\alpha \delta_\nu]^{\mathbf{R}^{\rho \mathbf{g}}}) \end{pmatrix}
\end{aligned} \tag{A24}$$

where no approximations have been taken so far.

APPENDIX B: APPROXIMATE FORM FOR THE REVERSIBLE DRIFT

We will now use the approximations (49) (52) in order to compute all the different terms that appear in the exact equations (43). Consider first the term

$$[\hat{\rho}\delta_\mu \nabla^\alpha \delta_\nu]^{R\rho g} = \int d\mathbf{r} \langle \hat{\rho}_\mathbf{r} \rangle^{R\rho g} \delta_\mu(\mathbf{r}) \nabla \delta_\mu(\mathbf{r}) \quad (B1)$$

By using the linear for spiky approximation (49) this becomes

$$[\hat{\rho}\delta_\mu \nabla^\alpha \delta_\nu]^{R\rho g} \simeq \int d\mathbf{r} \langle \psi_\sigma(\mathbf{r}) \hat{\rho}_\sigma \rangle^{R\rho g} \delta_\mu(\mathbf{r}) \nabla \delta_\mu(\mathbf{r}) \quad (B2)$$

Note that the conditional expectation of the discrete density field is just the conditioning value, this is $\langle \hat{\rho}_\sigma \rangle^{R\rho g} = \rho_\sigma$. Therefore,

$$[\hat{\rho}\delta_\mu \nabla^\alpha \delta_\nu]^{R\rho g} = \int d\mathbf{r} \psi_\sigma(\mathbf{r}) \rho_\sigma \delta_\mu \nabla \delta_\mu = \|\bar{\rho}\delta_\mu \nabla \delta_\mu\| \quad (B3)$$

where we have used the definition of the interpolated density field. By using the LFSAs (49) for the momentum field, the other required term becomes

$$[\hat{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu]^{R\rho g} \simeq \|\bar{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu\| \quad (B4)$$

In summary, the form of the reversible dynamics under the linear for spiky approximation is

$$\begin{pmatrix} \langle L\mathbf{R} \rangle^{R\rho g} \\ \langle L\rho_\mu \rangle^{R\rho g} \\ \langle L\mathbf{g}_\mu^\alpha \rangle^{R\rho g} \end{pmatrix} = \begin{pmatrix} 0 & 0 & \delta_\mu(\mathbf{R}) \\ 0 & 0 & \|\bar{\rho}\delta_\nu \nabla^\beta \delta_\mu\| \\ -\delta_\mu(\mathbf{R}) & -\|\bar{\rho}\delta_\mu \nabla^\alpha \delta_\nu\| & \|\bar{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu\| - \|\bar{\mathbf{g}}^\beta \delta_\mu \nabla^\alpha \delta_\nu\| \end{pmatrix} \begin{pmatrix} \frac{\partial \mathcal{H}}{\partial \mathbf{R}} \\ \frac{\partial \mathcal{H}}{\partial \rho_\nu} \\ \frac{\partial \mathcal{H}}{\partial \mathbf{g}_\nu^\beta} \end{pmatrix} - k_B T \begin{pmatrix} 0 \\ 0 \\ -\nabla^\alpha \delta_\mu(\mathbf{R}) \end{pmatrix} \quad (B8)$$

Let us now apply the linear for spiky approximation to the exact translation invariance identity (A14). By multiplying (B3) and (B6) with the volume \mathcal{V}_μ and sum over μ , by using (29), we obtain

$$\begin{aligned} \|\hat{\rho} \nabla^\alpha \delta_\nu\|^{R\rho g} &\simeq \|\bar{\rho} \nabla \delta_\mu\| \\ \frac{\partial}{\partial \rho_\nu} \|\hat{\rho} \nabla^\alpha \delta_\nu\|^{R\rho g} &\simeq 0 \end{aligned} \quad (B9)$$

By using these approximations in the exact translation property (A14) we obtain the approximation

$$\frac{\partial \mathcal{F}}{\partial \mathbf{R}} + \|\bar{\rho} \nabla \delta_\nu\| \frac{\partial \mathcal{F}}{\partial \rho_\nu} = 0 \quad (B10)$$

We see that, formally, the linear for spiky approximation approximate hatted functions with overlined functions, and allows to transform the double brackets $[\dots]^{R\rho g}$ into simple space averages $\|\dots\|$.

Consider now the derivative of these terms that are required in (A24)

$$\frac{\partial}{\partial \mathbf{g}_\nu^\alpha} \|\bar{\rho} \delta_\nu \nabla^\alpha \delta_\mu\| = 0 \quad (B5)$$

This vanishes because the mass density and momentum density variables are independent. The next term is of the form

$$\begin{aligned} \frac{\partial}{\partial \rho_\nu} \|\hat{\rho} \delta_\mu \nabla^\alpha \delta_\nu\|^{R\rho g} &\simeq \frac{\partial}{\partial \rho_\nu} \|\bar{\rho} \delta_\mu \nabla^\alpha \delta_\nu\| \\ &= \|\psi_\nu \delta_\mu \nabla^\alpha \delta_\nu\| = 0 \end{aligned} \quad (B6)$$

where the term vanishes due to (D7). Finally, we need to compute the following derivative

$$\begin{aligned} \frac{\partial}{\partial \mathbf{g}_\nu^\beta} \left([\hat{\mathbf{g}}^\alpha \delta_\nu \nabla^\beta \delta_\mu]^{R\rho g} - [\bar{\mathbf{g}}^\beta \delta_\mu \nabla^\alpha \delta_\nu]^{R\rho g} \right) \\ \simeq \frac{\partial}{\partial \mathbf{g}_\nu^\beta} \left(\mathbf{g}_\sigma^\alpha \|\psi_\sigma \delta_\nu \nabla^\beta \delta_\mu\| - \mathbf{g}_\sigma^\beta \|\psi_\sigma \delta_\mu \nabla^\alpha \delta_\nu\| \right) \\ = \|\psi_\nu \delta_\nu \nabla^\alpha \delta_\mu\| - 3 \|\psi_\nu \delta_\mu \nabla^\alpha \delta_\nu\| = 0 \end{aligned} \quad (B7)$$

where the terms vanish due to (D7).

APPENDIX C: APPROXIMATE MODEL FOR THE CG HAMILTONIAN

a. Modelling the kinetic part of the CG Hamiltonian

The kinetic part of exact CG Hamiltonian in (A11) can be approximated under the LFSAs (52) in the form

$$\begin{aligned} &-k_B T \ln \left\langle \frac{\exp \left\{ -\frac{\beta}{2} \mathbf{g}_\mu \hat{M}_{\mu\nu}^{-1} \mathbf{g}_\nu \right\}}{(2\pi/\beta)^{3M/2} \det \hat{M}^{3/2}} \right\rangle^{R\rho} \\ &\simeq \frac{1}{2} \mathbf{g}_\mu \bar{M}_{\mu\nu}^{-1} \mathbf{g}_\nu + \frac{3k_B T}{2} \ln \det \bar{M} \end{aligned} \quad (C1)$$

up to irrelevant constant terms. The order of magnitude of the term proportional to $k_B T$ can be estimate by assuming a sufficiently smooth density field for which we

may approximate

$$\mathcal{M}_{\mu\nu} = (\delta_\mu \delta_\nu \psi_\sigma) \rho_\sigma \simeq \delta_{\mu\nu} \frac{\rho_\mu}{\mathcal{V}_\mu} \quad (\text{C2})$$

leading to a diagonal matrix. This approximation still satisfies the exact requirement (51). The $\log \det$ term of a diagonal matrix is simple

$$\frac{3k_B T}{2} \ln \det \mathcal{M} = \frac{3k_B T}{2} \text{tr} \ln \mathcal{M} \simeq \frac{3k_B T}{2} \sum_\mu \ln \rho_\mu \quad (\text{C3})$$

We observe that this term is *not extensive*, this is, does not scale as the number of particles per node. On the other hand, the kinetic energy

$$\frac{1}{2} \mathbf{g}_\mu \overline{M}_{\mu\nu}^{-1} \mathbf{g}_\nu \simeq \sum_\mu \mathcal{V}_\mu \frac{\mathbf{g}_\mu^2}{\rho_\mu} \quad (\text{C4})$$

scales with the number of particles per node because, typically $\mathbf{g}_\mu \sim \rho_\mu \mathbf{v}_\mu$ and $\rho_\mu \sim m \frac{N_\mu}{\mathcal{V}_\mu}$, giving

$$\frac{1}{2} \mathbf{g}_\mu \overline{M}_{\mu\nu}^{-1} \mathbf{g}_\nu \sim \sum_\mu \frac{N_\mu m}{2} \mathbf{v}_\mu^2 \quad (\text{C5})$$

which is an extensive quantity, proportional to the number of particles per node. As we assume that the typical number of particles per node is large, we may neglect the term $\frac{3k_B T}{2} \ln \det \mathcal{M}$ in front of the kinetic energy term.

From now on we will neglect this term and the CG Hamiltonian has the form

$$\mathcal{H}(\mathbf{R}, \rho, \mathbf{g}) = \frac{1}{2} \mathbf{g}_\mu \overline{M}_{\mu\nu}^{-1} \mathbf{g}_\nu + \mathcal{F}(\mathbf{R}, \rho) + \Phi^{\text{ext}}(\mathbf{R}) \quad (\text{C6})$$

We will need the derivatives of the CG Hamiltonian that are given by

$$\begin{aligned} \frac{\partial \mathcal{H}}{\partial \mathbf{R}} &= \frac{\partial \mathcal{F}}{\partial \mathbf{R}} + \frac{\partial \Phi^{\text{ext}}}{\partial \mathbf{R}} \\ \frac{\partial \mathcal{H}}{\partial \rho_\mu} &= \frac{1}{2} \mathbf{g}_{\mu'} \frac{\partial \overline{M}_{\mu'\nu'}^{-1}}{\partial \rho_\mu} \mathbf{g}_{\nu'} + \frac{\partial \mathcal{F}}{\partial \rho_\mu} \\ \frac{\partial \mathcal{H}}{\partial \mathbf{g}_\mu} &= \overline{M}_{\mu\mu'}^{-1} \mathbf{g}_{\mu'} \end{aligned} \quad (\text{C7})$$

We now use the result

$$\begin{aligned} \frac{\partial \overline{M}_{\mu'\nu'}^{-1}}{\partial \rho_\mu} &= -\overline{M}_{\mu'\mu''}^{-1} \frac{\partial \overline{M}_{\mu''\nu''}}{\partial \rho_\mu} \overline{M}_{\nu''\nu'}^{-1} \\ &= -\overline{M}_{\mu'\mu''}^{-1} \|\delta_{\mu''} \psi_\mu \delta_{\nu''}\| \overline{M}_{\nu''\nu'}^{-1} \end{aligned} \quad (\text{C8})$$

where we have used the explicit form of the matrix in (53). With the discrete velocity (59) the derivatives (C7)

become, finally

$$\begin{aligned} \frac{\partial \mathcal{H}}{\partial \mathbf{R}} &= \frac{\partial \mathcal{F}}{\partial \mathbf{R}} + \frac{\partial \Phi^{\text{ext}}}{\partial \mathbf{R}} \\ \frac{\partial \mathcal{H}}{\partial \rho_\mu} &= -\frac{1}{2} \|\psi_\mu \overline{\mathbf{v}\mathbf{v}}\| + \frac{\partial \mathcal{F}}{\partial \rho_\mu} \\ \frac{\partial \mathcal{H}}{\partial \mathbf{g}_\mu} &= M_{\mu\mu'}^\psi \mathbf{v}_{\mu'} \end{aligned} \quad (\text{C9})$$

b. Modelling the solvent part of the free energy

The free energy of the solvent $\mathcal{F}^{\text{sol}}(\rho)$ is obtained from the first equation (A10) from the probability (A8). The explicit calculation of $P_{\text{sol}}^{\text{eq}}(\rho)$ is in general impossible due to the high dimensionality of the integrals in phase space. Therefore, we are forced to consider specific approximate models for this probability distribution.

In accordance with the assumption that each hydrodynamic cell contains many fluid molecules, we will assume that the probability $P_{\text{sol}}^{\text{eq}}(\rho)$ is a Gaussian. The Gaussian probability has the form

$$P_{\text{sol}}^{\text{eq}}(\rho) = \frac{1}{N} \exp \left\{ -\frac{1}{2} \delta \rho_\mu C_{\mu\nu}^{-1} \delta \rho_\nu \right\} \quad (\text{C10})$$

where N is the normalization, $\delta \rho_\mu = \rho_\mu - \rho_{\text{eq}}$ are the fluctuations with respect to the homogeneous density ρ_{eq} , and the matrix of covariances is given by

$$C_{\mu\nu} = \langle \delta \rho_\mu \delta \rho_\nu \rangle_{\text{eq}} = \int d\mathbf{r} \int d\mathbf{r} \delta_\mu(\mathbf{r}) \delta_\nu(\mathbf{r}') \langle \delta \rho_\mathbf{r} \delta \rho_{\mathbf{r}'} \rangle_{\text{eq}} \quad (\text{C11})$$

We estimate the form of this matrix as follows. We assume that the correlation of density fluctuations fluctuations decay in a length scale much smaller than the size of the cell and, therefore, the correlation can be approximated as proportional to the Dirac delta function, according to a standard result

$$\langle \delta \rho_\mathbf{r} \delta \rho_{\mathbf{r}'} \rangle_{\text{eq}} = \frac{k_B T \rho_{\text{eq}}}{c^2} \delta(\mathbf{r} - \mathbf{r}') \quad (\text{C12})$$

where c is the isothermal speed of sound. The resulting free energy is quadratic in the density and will be termed *Gaussian free energy*. It has the explicit form

$$\mathcal{F}^{\text{sol}}(\rho) = \frac{c^2}{2 \rho_{\text{eq}}} \delta \rho_\mu M_{\mu\nu}^\psi \delta \rho_\nu \quad (\text{C13})$$

This free energy *function* can be obtained from a local free energy *functional* of the form (square brackets denote a functional, while rounded parenthesis denote a function)

$$\mathcal{F}^{\text{sol}}[\rho] = \int d\mathbf{r} f^{\text{sol}}(\rho(\mathbf{r})) \quad (\text{C14})$$

where $f^{\text{sol}}(\rho)$ is the thermodynamic free energy density of the solvent which, for the Gaussian model is

$$f(\rho) = \frac{c^2}{2\rho_{\text{eq}}} (\rho - \rho_{\text{eq}})^2 \quad (\text{C15})$$

This functional is perhaps the simplest model familiar from Density Functional Theory. The model neglects molecular correlations, which is appropriate for the coarse description in which the hydrodynamic cells are much larger than molecular correlation lengths. The free energy (C13) is obtained from the functional (C14)-(C15) by using the interpolated field $\bar{\rho}(\mathbf{r}) = \rho_\sigma \psi_\sigma(\mathbf{r})$ in the functional, as advocated in Ref. [47].

Once we have a free energy density, we may compute the pressure of the Gaussian model from the well-known thermodynamic relation

$$P^{\text{sol}}(\rho) = \rho \frac{df^{\text{sol}}}{d\rho}(\rho) - f^{\text{sol}}(\rho) \quad (\text{C16})$$

The pressure (C16) that corresponds to (C15) is given by the quadratic equation of state (EOS)

$$P^{\text{sol}}(\rho) = \frac{c^2}{2\rho_{\text{eq}}} (\rho^2 - \rho_{\text{eq}}^2) \quad (\text{C17})$$

Observe that for small deviations from equilibrium we obtain the expected linear EOS $P^{\text{sol}}(\rho) = c^2 (\rho - \rho_{\text{eq}})$.

c. Modelling the interaction part of the free energy

The interaction part of the free energy has the exact microscopic expression given in (48). We may obtain a simple model for this function if we consider the linear for spiky approximation (49). Note that the microscopic potential energy of interaction between the nanoparticle and the solvent molecules can be expressed in terms of the microscopic solvent mass density as

$$\sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} - \mathbf{q}_i) = \frac{1}{m} \int d\mathbf{r} \Phi^{\text{int}}(\mathbf{R} - \mathbf{r}) \hat{\rho}_{\mathbf{r}}^{\text{sol}}(z) \quad (\text{C18})$$

Within the linear for spiky approximation, we will approximate the spiky field $\hat{\rho}_{\mathbf{r}}^{\text{sol}}(z)$ with a linear interpolation

$$\hat{\rho}_{\mathbf{r}}^{\text{sol}}(z) \simeq \psi_\mu(\mathbf{r}) \hat{\rho}_\mu^{\text{sol}}(z) \quad (\text{C19})$$

by using the approximation (C19) into (C18) we obtain

$$\sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} - \mathbf{q}_i) \simeq \frac{1}{m} \Phi_\mu^{\text{int}}(\mathbf{R}) \hat{\rho}_\mu^{\text{sol}}(z) \quad (\text{C20})$$

where the nodal potential $\Phi_\mu^{\text{int}}(\mathbf{R})$ is defined according to

$$\Phi_\mu^{\text{int}}(\mathbf{R}) \equiv \int d\mathbf{r} \Phi^{\text{int}}(\mathbf{R} - \mathbf{r}) \psi_\mu(\mathbf{r}) \quad (\text{C21})$$

We consider situations in which the nanoparticle is much smaller than the hydrodynamic cells and the range of the interaction potential $\Phi^{\text{int}}(\mathbf{R} - \mathbf{r})$ is also much smaller than the support of $\psi_\mu(\mathbf{r})$. Therefore, we may approximate $\psi_\mu(\mathbf{r}) \simeq \psi_\mu(\mathbf{R})$ in Eq. (C21), leading to

$$\Phi_\mu^{\text{int}}(\mathbf{R}) \simeq a \psi_\mu(\mathbf{R}) \quad (\text{C22})$$

where the constant a is the volume integral of the interaction potential

$$a = \int d\mathbf{r} \Phi^{\text{int}}(\mathbf{r}) \equiv \frac{m m_0 c_0^2}{\rho_{\text{eq}}} \quad (\text{C23})$$

and we have introduced the “particle speed of sound” c_0 whose physical interpretation is that it gives the strength of the interaction of the nanoparticle with the solvent particles. Under these approximations, the microscopic potential of interaction between the nanoparticle and the solvent molecules is approximated by

$$\sum_{i=1}^N \Phi^{\text{int}}(\mathbf{R} - \mathbf{q}_i) \simeq \frac{m_0 c_0^2}{\rho_{\text{eq}}} \psi_\mu(\mathbf{R}) \hat{\rho}_\mu^{\text{sol}}(z) \quad (\text{C24})$$

Note that this approximation breaks translation invariance, because while the left hand side of (C24) is invariant under a translation of all the particles, the right hand side is not. In the approximation (C24), the potential energy of the nanoparticle depends on the microscopic configuration z of the solvent particles only through the discrete solvent number density $\hat{n}_\mu^{\text{sol}}(z)$. Therefore, by substituting the approximation (C24) for the potential energy into the interaction part of the free energy (48) we obtain the explicit model

$$\mathcal{F}^{\text{int}}(\mathbf{R}, \rho^{\text{sol}}) \simeq \frac{m_0 c_0^2}{\rho_{\text{eq}}} \psi_\mu(\mathbf{R}) \rho_\mu^{\text{sol}} \quad (\text{C25})$$

By collecting (C13) and (C25) the free energy (A12) becomes

$$\mathcal{F}(\mathbf{R}, \rho) = \frac{c^2}{2\rho_{\text{eq}}} \delta \rho_\mu^{\text{sol}} M_{\mu\nu}^\psi \delta \rho_\nu^{\text{sol}} + \frac{m_0 c_0^2}{\rho_{\text{eq}}} \psi_\mu(\mathbf{R}) \delta \rho_\mu^{\text{sol}} \quad (\text{C26})$$

In terms of the total mass density, the free energy is

$$\begin{aligned} \mathcal{F}(\mathbf{R}, \rho) = & \frac{c^2}{2\rho_{\text{eq}}} \delta \rho_\mu M_{\mu\nu}^\psi \delta \rho_\nu + \frac{m_0 (c_0^2 - c^2)}{\rho_{\text{eq}}} \psi_\mu(\mathbf{R}) \delta \rho_\mu \\ & + \epsilon(\mathbf{R}) \end{aligned} \quad (\text{C27})$$

where the last term is a density-independent term

$$\epsilon(\mathbf{R}) \equiv \frac{m_0^2}{\rho_{\text{eq}}} \left[\frac{c^2}{2} - c_0^2 \right] \delta_\mu(\mathbf{R}) \psi_\mu(\mathbf{R}) \quad (\text{C28})$$

The derivatives of the model (C27) are

$$\begin{aligned} \frac{\partial}{\partial \mathbf{R}} \mathcal{F}(\mathbf{R}, \rho) &= \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \rho_\mu \nabla \psi_\mu(\mathbf{R}) + \frac{\partial \epsilon}{\partial \mathbf{R}}(\mathbf{R}) \\ \frac{\partial}{\partial \rho_\mu} \mathcal{F}(\mathbf{R}, \rho) &= \frac{c^2}{\rho_{\text{eq}}} M_{\mu\nu}^\psi \delta \rho_\nu + \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \psi_\mu(\mathbf{R}) \end{aligned} \quad (\text{C29})$$

From Eq. (A20) the force on the nanoparticle due to the surrounding solvent is given by

$$\begin{aligned} \mathbf{F}(\mathbf{R}) &= -\frac{\partial \mathcal{F}}{\partial \mathbf{R}}(\mathbf{R}, \rho) - m_0 \nabla \delta_\nu(\mathbf{R}) \frac{\partial \mathcal{F}}{\partial \rho_\nu}(\mathbf{R}, \rho) \\ &= -\frac{m_0 c_0^2}{\rho_{\text{eq}}} \rho_\mu^{\text{sol}} \nabla \psi_\mu(\mathbf{R}) \end{aligned} \quad (\text{C30})$$

This form of the force is consistent with the approximation (C24).

We now consider the translation invariance (66) property of the free energy. This property is a strong guiding principle for the modelling of the free energy. In order to see if this important property is satisfied, we compute

$$\begin{aligned} &\frac{\partial}{\partial \mathbf{R}} \mathcal{F}(\mathbf{R}, \rho) + \|\bar{\rho} \nabla \delta_\nu\| \frac{\partial \mathcal{F}}{\partial \rho_\nu} \\ &= \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \rho_\mu (\nabla \psi_\mu(\mathbf{R}) + \|\psi_\mu \nabla \delta_\nu\| \psi_\nu(\mathbf{R})) \\ &+ \frac{c^2}{\rho_{\text{eq}}} \underbrace{\|\bar{\rho} \nabla \bar{\rho}\|}_{=0} + \frac{\partial \epsilon}{\partial \mathbf{R}}(\mathbf{R}) \\ &= \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} (\nabla \bar{\rho}(\mathbf{R}) - \|\Delta \nabla \bar{\rho}\|) + \frac{\partial \epsilon}{\partial \mathbf{R}}(\mathbf{R}) \end{aligned} \quad (\text{C31})$$

where we used that in a periodic domain $\|\bar{\rho} \nabla \bar{\rho}\| = 0$ (as can be seen from integration by parts). Also, $\|\Delta \nabla \bar{\rho}\|$ is a compact notation for

$$\|\Delta \nabla \bar{\rho}\| \equiv \int d\mathbf{r} \Delta(\mathbf{R}, \mathbf{r}) \nabla \bar{\rho}(\mathbf{r}) \quad (\text{C32})$$

and it depends on the position \mathbf{R} of the nanoparticle. We observe that, in general, (C31) does not vanish. However, note that for sufficiently smooth density fields Eq (67) applies, and the first term is small. In particular, in the incompressible limit in which the density is constant, it vanishes identically. This strongly suggests that for modelling purposes, it is convenient to set $\epsilon(\mathbf{R}) = 0$ and correct the free energy model developed so far in order to better respect translational invariance.

In conclusion, in the present work we will use the following model for the free energy of a fluid made of a

solvent interacting with a single nanoparticle

$$\mathcal{F}(\mathbf{R}, \rho) = \frac{c^2}{2\rho_{\text{eq}}} \delta \rho_\mu M_{\mu\nu}^\psi \delta \rho_\nu + \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \psi_\mu(\mathbf{R}) \rho_\mu \quad (\text{C33})$$

Because this free energy gives the probability $P(\mathbf{R}, \rho)$, and we expect that for the case that the nanoparticle is identical to a tagged solvent particle this probability is Gaussian, we conclude that the limit of the nanoparticle becoming just another solvent particle is realized for $c_0 = c$.

The derivatives of the free energy model (C33) are

$$\begin{aligned} \frac{\partial}{\partial \mathbf{R}} \mathcal{F}(\mathbf{R}, \rho) &= \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \rho_\mu \nabla \psi_\mu(\mathbf{R}) \\ \frac{\partial}{\partial \rho_\mu} \mathcal{F}(\mathbf{R}, \rho) &= \frac{c^2}{\rho_{\text{eq}}} M_{\mu\nu}^\psi \delta \rho_\nu + \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \psi_\mu(\mathbf{R}) \end{aligned} \quad (\text{C34})$$

With these derivatives, we now compute the term (68) entering the momentum equation

$$\begin{aligned} &-\delta_\mu(\mathbf{R}) \frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \|\bar{\rho} \delta_\mu \nabla \delta_\nu\| \frac{\partial \mathcal{F}}{\partial \rho_\nu} \\ &= -\frac{c^2}{\rho_{\text{eq}}} \|\delta_\mu \bar{\rho} \nabla \bar{\rho}\| - \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} (\delta_\mu(\mathbf{R}) \nabla \bar{\rho}(\mathbf{R}) + \|\bar{\rho} \delta_\mu \nabla \Delta\|) \\ &= -\|\delta_\mu \nabla \bar{P}\| - \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} (\delta_\mu(\mathbf{R}) \nabla \bar{\rho}(\mathbf{R}) - \|\delta_\mu \Delta \nabla \bar{\rho}\|) \end{aligned} \quad (\text{C35})$$

where we have introduced the following total pressure equation of state

$$\bar{P}(\mathbf{r}) \equiv \frac{c^2}{2\rho_{\text{eq}}} (\bar{\rho}(\mathbf{r})^2 - \rho_{\text{eq}}^2) + \frac{m_0(c_0^2 - c^2)}{\rho_{\text{eq}}} \Delta(\mathbf{R}, \mathbf{r}) \bar{\rho}(\mathbf{r}) \quad (\text{C36})$$

Note that in the limit when the nanoparticle is just a tagged solvent particle we have $c_0 = c$ and the last contribution to the pressure vanishes, giving simply the pressure of the Gaussian model. The last term in (C35) is arguably small and will be neglected. Indeed, for smooth density fields

$$\|\delta_\mu \Delta \nabla \bar{\rho}\| \simeq \|\delta_\mu \Delta \|\nabla \bar{\rho}(\mathbf{R}) = \delta_\mu(\mathbf{R}) \nabla \bar{\rho}(\mathbf{R}) \quad (\text{C37})$$

and we have, finally

$$-\delta_\mu(\mathbf{R}) \frac{\partial \mathcal{F}}{\partial \mathbf{R}} - \|\bar{\rho} \delta_\mu \nabla \delta_\nu\| \frac{\partial \mathcal{F}}{\partial \rho_\nu} = -\|\delta_\mu \nabla \bar{P}\| \quad (\text{C38})$$

1. Translation invariance and the barometric law

In this appendix we examine the marginal probability $P^{\text{eq}}(\mathbf{R})$ of finding the nanoparticle at position \mathbf{R} . This

probability is, by definition,

$$\begin{aligned} P^{\text{eq}}(\mathbf{R}) &= \int d\rho P^{\text{eq}}(\mathbf{R}, \rho) \\ &= \int d\rho \exp\{-\beta (\mathcal{F}(\mathbf{R}, \rho) + \Phi^{\text{ext}}(\mathbf{R}))\} \end{aligned} \quad (\text{C39})$$

Take its gradient

$$\begin{aligned} \frac{\partial}{\partial \mathbf{R}} P^{\text{eq}}(\mathbf{R}) &= -\beta \int d\rho \frac{\partial \mathcal{F}}{\partial \mathbf{R}} \exp\{-\beta (\mathcal{F}(\mathbf{R}, \rho) + \Phi^{\text{ext}}(\mathbf{R}))\} \\ &\quad - \beta \frac{\partial \Phi^{\text{ext}}}{\partial \mathbf{R}} P^{\text{eq}}(\mathbf{R}) \end{aligned} \quad (\text{C40})$$

and use the approximate translation invariance of the free energy (66)

$$\begin{aligned} &\frac{\partial}{\partial \mathbf{R}} P^{\text{eq}}(\mathbf{R}) + \beta \frac{\partial \Phi^{\text{ext}}}{\partial \mathbf{R}} P^{\text{eq}}(\mathbf{R}) \\ &= \beta \int d\rho \|\bar{\rho} \nabla \delta_\mu\| \frac{\partial \mathcal{F}}{\partial \rho_\mu} \exp\{-\beta (\mathcal{F}(\mathbf{R}, \rho) + \Phi^{\text{ext}}(\mathbf{R}))\} \\ &= \int d\rho \exp\{-\beta (\mathcal{F}(\mathbf{R}, \rho) + \Phi^{\text{ext}}(\mathbf{R}))\} \frac{\partial}{\partial \rho_\mu} \|\bar{\rho} \nabla \delta_\mu\| \\ &= \int d\rho \exp\{-\beta \mathcal{F}\} \|\psi_\mu \nabla \delta_\mu\| = 0 \end{aligned} \quad (\text{C41})$$

Therefore, the (approximate) translation invariance property (66) rigorously implies the well-known barometric law

$$P^{\text{eq}}(\mathbf{R}) = \frac{1}{Q} \exp\{-\beta \Phi^{\text{ext}}(\mathbf{R})\} \quad (\text{C42})$$

where Q is the normalization factor. In the absence of an external field the probability to find the particle at a particular point \mathbf{R} should be constant.

Should the free energy model respect *exactly* the translation invariance property (66), then the marginal distribution function would be *rigorously* given by the barometric law (C42). However, the Gaussian model (C33) for the free energy satisfies (66) only approximately, up to second order terms. As a consequence, the marginal distribution $P^{\text{eq}}(\mathbf{R})$ corresponding to the model (C33) does not give *exactly* the barometric law (C42) but rather

$$\begin{aligned} P^{\text{eq}}(\mathbf{R}) &= \int d\rho \exp\{-\beta \mathcal{F}(\mathbf{R}, \rho) - \beta \Phi^{\text{ext}}(\mathbf{R})\} \\ &\propto \exp\left\{-\beta \Phi^{\text{ext}}(\mathbf{R}) + \beta \frac{m_0^2 (c_0^2 - c^2)^2}{2\rho_{\text{eq}} c^2} \delta_\mu(\mathbf{R}) \psi_\mu(\mathbf{R})\right\} \end{aligned} \quad (\text{C43})$$

as can be seen by explicitly performing the Gaussian integral. When $\Phi^{\text{ext}} = 0$, the nanoparticle is not homogeneously distributed in space but, rather, “sees” the underlying grid, unless it is a tagged fluid particle in which case $c_0 = c$.

APPENDIX D: DERIVATIVES OF THE BASIS FUNCTIONS

In this work we assume periodic boundary conditions. Therefore any integration by parts give no surface terms. For example

$$\|A \nabla B\| = -\|B \nabla A\| \quad (\text{D1})$$

for arbitrary functions $A(\mathbf{r}), B(\mathbf{r})$.

We consider some identities that involve gradients of basis functions. For example, note that

$$\begin{aligned} \|\delta_\mu \psi_\nu \nabla \delta_\nu\| &= \|\delta_\mu \delta_\nu \nabla \psi_\nu\| = -\|\psi_\nu \nabla \delta_\mu \delta_\nu\| \\ &= -\|\psi_\nu \delta_\mu \nabla \delta_\nu\| - \|\psi_\nu \delta_\nu \nabla \delta_\mu\| \end{aligned} \quad (\text{D2})$$

where in the second identity we have performed an integration by parts. Therefore,

$$\|\psi_\nu \delta_\nu \nabla \delta_\mu\| = -2\|\delta_\mu \psi_\nu \nabla \delta_\nu\| \quad (\text{D3})$$

By multiplying both sides of this equation with \mathcal{V}_μ and summing over μ , we obtain

$$\|\delta_\nu \nabla \psi_\nu\| = 0 \quad (\text{D4})$$

Another identity is obtained by introducing the following vector defined at each node μ

$$\mathbf{a}_\mu \equiv \|\delta_\mu \psi_\nu \nabla \delta_\nu\| \quad (\text{D5})$$

Because of (D4), this vector satisfies

$$\mathcal{V}_\mu \mathbf{a}_\mu = 0 \quad (\text{D6})$$

If the mesh of nodes is regular in such a way that for all nodes μ we have $\mathbf{a}_\mu = \mathbf{a}_0$, then the above equation implies $\mathbf{a}_0 = 0$. Therefore, in regular grids we have the identities

$$\begin{aligned} \|\psi_\nu \delta_\nu \nabla \delta_\mu\| &= 0 \\ \|\delta_\mu \psi_\nu \nabla \delta_\nu\| &= 0 \end{aligned} \quad (\text{D7})$$

It is expected that in non-regular meshes these quantities are also zero or very small.

APPENDIX E: MOMENTUM INTEGRALS

In this appendix we quote the results for the following momentum integrals

$$\begin{aligned} I_0(\mathbf{g}) &\equiv \int \prod_{i=0}^N d\mathbf{p}_i \exp \left\{ -\beta \sum_{i=0}^N \frac{\mathbf{p}_i^2}{2m_i} \right\} \\ &\quad \times \prod_{\mu}^M \delta \left(\sum_{i=0}^N \mathbf{p}_i \delta_{\mu}(\mathbf{q}_i) - \mathbf{g}_{\mu} \right) \\ &= \frac{\prod_{i=0}^N (2\pi m_i k_B T)^{3/2}}{(2\pi k_B T)^{3M/2} \det \hat{M}^{3/2}} \exp \left\{ -\frac{\beta}{2} \mathbf{g}_{\mu} \hat{M}_{\mu\nu}^{-1} \mathbf{g}_{\nu} \right\} \end{aligned} \quad (\text{E1})$$

$$\begin{aligned} \mathbf{I}_i^{(1)}(\mathbf{g}) &\equiv \int \prod_{i=0}^N d\mathbf{p}_i \exp \left\{ -\beta \sum_{i=0}^N \frac{\mathbf{p}_i^2}{2m_i} \right\} \\ &\quad \times \prod_{\mu}^M \delta \left(\sum_{i=0}^N \mathbf{p}_i \delta_{\mu}(\mathbf{q}_i) - \mathbf{g}_{\mu} \right) \mathbf{p}_i \\ &= I_0(\mathbf{g}) m_i \delta_{\mu}(\mathbf{q}_i) \hat{M}_{\mu\nu}^{-1} \mathbf{g}_{\nu} \end{aligned} \quad (\text{E2})$$

where the configuration dependent mass matrix is defined as

$$\hat{M}_{\mu\nu}(z) \equiv \sum_{i=0}^N m_i \delta_{\mu}(\mathbf{q}_i) \delta_{\nu}(\mathbf{q}_i) \quad (\text{E3})$$

The above integrals are relatively easy to compute by using the Fourier representation of the Dirac delta function.

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